A SCHOOL CERTIFICATE CHEMISTRY COURSE

BY

J. T. FREEMAN, M.B.E., B.Sc., Ph.D., F.R.I.C.

BLACKIE & SON LIMITED

First published 1943

PREFACE

This book presents the subject in simple, straightforward language. Simplicity is also aimed at in the drawings, which can easily be made by the non-artistic pupil, equipped with pencil and ruler. It is hoped that the same simplicity appears in the questions given. They are straightforward questions on the pupils' knowledge of the text, and contain no " frills ". They are not intended to take the place of selected School Certificate (General Certificate of Education—Ordinary Level) questions.

Industrial processes and everyday applications are brought in, as much as possible. Constant reference in these directions should play a large part in the teaching of the subject, which is often treated in much too theoretical a way. The authors are grateful to various firms which have helped in supplying material for blocks. They regret that they are unable to make use of much excellent material, owing to war-time restrictions.

It is hoped that pupils will be encouraged to *read* the book, and not to use it merely as a reference, and as an aid in doing " prep ". The subject is presented in its logical sequence: but most teachers will prefer to leave much of the physical chemistry until the pupil has acquired some little knowledge of the facts of chemistry. It is suggested that a final reading should be made, and that this should be straight through the book.

Inorganic Chemistry, to School Certificate (General Certificate of Education—Ordinary Level) standard, in

spite of the interest created among the pupils by their performing their own experiments, is not an easy subject to teach, if the full benefit of its training value is to be obtained. In later stages, especially in Organic Chemistry, the subject becomes easier to teach, because the underlying principles are more apparent, and the unity and coherence of the subject becomes clear. Because of this, it seems certain that more skill in teaching and even more enthusiasm on the part of the teacher are required than are demanded by Physics. No textbook on elementary Chemistry, however fully — and often colloquially — written, can take the place of a keen and competent teacher. Given the latter, all that is necessary is that the textbook cover the subject-matter fully and clearly, and it is hoped that this book does that.

P. T. F.
J. L. St. J.

CHAPTER I

THE SCIENCE OF CHEMISTRY

If your study of chemistry — even of elementary chemistry — succeeds in giving you nothing more than a knowledge of the *facts* which you learn, however interesting in themselves these may be, it fails in its object. If it does not succeed in calling out the scientific spirit which is in you, you may pass examinations by writing down the facts, but you will not awaken a spirit which can do much to influence your whole outlook on life. What is this spirit?

It is always present in small children. You probably cannot remember the time when you yourself wanted to know all about everything of which your senses made you aware: but you have probably had dealings with small boys or girls aged, say, three or four years, and have noticed how they sometimes drive older people nearly crazy by their incessant questioning. They *want to know*. They are curious. All of them lose some of this curiosity as they grow older, and teachers sometimes regret that many of their pupils seem to have lost most of it.

Have you thought that we owe almost all of the comforts of life to the curiosity of people in the past? They *wanted to know*. The process by which they found out what they wanted to know is called *research*, and is going on unceasingly in all directions to-day. If the object is to find out the secrets of nature — that is, of the world around us — we call it scientific research. There are other kinds, such as literary or historical research. But it is to be noted that the object of all true research workers

is to get to know *the truth, for its own sake.* Such a discovery may or may not lead to some profit-making device. If it does, it is generally exploited by the business man and the inventor, and not by the discoverer. But the true research worker generally does not mind about that. He is engaged in one of the most absorbing and fascinating pursuits which man can undertake — he is treading where no man has trodden before.

The great Faraday, whose discoveries have done more to change the material conditions of life than those of any other single person, was one day showing to a lady friend a discovery (about a wire in a magnetic field) which was to lead to all of the marvels of modern electrical engineering — the dynamo, electric motor, electric lighting and heating, wireless, and so on. He himself little thought that all this would follow from his work. If he could come back to-day, more than a hundred years later, and see the transformations due to his work, he would be amazed. Yet he must have suspected something, for, when his friend asked, " Yes, it's very interesting, Professor Faraday, but what is the *use* of it?" he gave the reply, " Madam, what is the use of a newly-born baby?"

Faraday could have become very rich, but he always said that he had sufficient for his simple needs, and that he preferred to live simply in his rooms at the Royal Institution and continue his search for truth for its own sake. More than two thousand years previously, Aristotle had said that there is no nobler calling than the pursuit of knowledge for its own sake. This is the spirit of the true research worker.

Science, the study of the world around us, is one " subject ", though, for convenience, it is divided into a number of branches. There is physics, the study of how things move, of heat, light, sound, magnetism, electricity: zoology, the study of animals: botany, the study of plants: astronomy, the study of the heavenly bodies: and so on. But they all interlock with one

another. Chemistry and physics underlie the study of botany, zoology, and astronomy.

It must be emphasized that the seeker after the truth in science asks his questions of the object being studied. The professors of physics in Italy, nearly two thousand years after the time of Aristotle, were still blindly teaching the sayings of that philosopher, who, great as he was, did not always appeal to experiments in his search for the truth. He did not always ask the question of the actual object. For example, he had said, and the professors in Pisa continued to teach, that if two weights, one, say, five times as heavy as the other, were dropped at the same moment from a height, the heavier one would fall five times as fast as the other. This seems to be what one would expect. But the young professor Galileo stoutly denied this, and was cordially disliked by the older professors. They said, "How can that be? Don't you know what Aristotle said? Here it is, written quite plainly for anybody to read." Galileo replied, "I don't deny that that is what Aristotle said: but the *weights* don't say so. I'll show you." Accordingly, he dropped the weights from the famous Leaning Tower of Pisa, in front of them. Everybody could see that the weights reached the ground together. But the older professors *did not want to believe*. So they invented reasons why the weights had behaved in that peculiar way on that particular occasion.

If the scientist gets no answer when he asks the questions of the object of his study, he can ask again more closely, or (by varying the procedure of his experiment) in a different way. Yet, in spite of the tremendous extension of the knowledge of science in the last hundred years, there are very many questions to which we do not know the answers. Anybody who teaches the most elementary biology is continuously aware that if some small boy or girl asks him, "How does it happen?" he must honestly answer, "I don't know. No man knows."

Many of the quite simple experiments described in

this book, some of which you will, no doubt, perform in the laboratory, appear to be fully understood. Yet there are still secrets in them which no man has yet discovered. When you do them, or see them done, be *curious* about everything. Watch everything most intently. It is extraordinary how much is missed or inaccurately observed by people who have not trained their powers of observation. Two quite honest witnesses in a court of law, describing some quite ordinary happening which both of them saw clearly, often give two entirely different accounts. *Watch* the experiment *closely*. Jot down what you see, at once, if you think there is a chance that you may forget it, or "misremember" it. You may notice something which has not been observed before in all the thousands of times that the experiment has been performed. If possible, seek for the answers yourself. If not, ask about them. But never give up the quest for the truth for its own sake.

We begin, then, on chemistry, the science which inquires into the composition of the substances on and in the earth, the sea, the air, and the stars and planets, discovers how substances may be changed into other substances, and builds up evidence that all this is part of an ordered plan.

Chemistry can generally answer for you the question which, spoken or unspoken, you so often ask: "What is it made of?" and often: "How is it made?" If a chemist wants to know the answer to the first question, he has to split the substance up, and identify the resulting substances. This process is called *analysis*. He is then often in a position to answer the second question, either by taking these resulting substances and building up from them the original substance, or by building it up from other substances whose composition he knows. This is called *synthesis*. Both processes are essential, if the composition of a substance is to be thoroughly understood.

You know the dye indigo. It is a very valuable dark

blue dye, which resists the action of soap and light. It was formerly obtained solely from the leaves of a plant which grows in India and Java. Years ago, the demand for indigo far exceeded the supply from this plant. The substance was accordingly analysed. This is a difficult process, for not only had the "stuff of which it is made" to be determined, but also the way in which that stuff is arranged. A survey was then made of cheap and easily obtainable substances whose composition was known, and one was finally selected from which the indigo could be synthesized. This was naphthalene, familiar to you in the form of "moth balls", and a by-product in the distillation of coal tar. There are now other methods, and the result has been that the cultivation of the indigo plant has fallen off very considerably.

In a similar way, a great many substances previously obtainable only from plants and animals have been subjected to these two processes, and are now manufactured from substances not obtained from plants or animals. Thus, the flavouring of your "pineapple drops" is not pineapple juice, but is synthetic. That is not to say that it is harmful. Very many perfumes are synthetic. So are most dyes. Rubber has been analysed and many attempts have been made to synthesize it. For some purposes synthetic rubber has not proved as satisfactory as natural rubber. It is probable, however, that this state of affairs will not be permanent, and that synthetic rubber will eventually be obtained in a form as good and as cheap as the natural product. Green plants, in daylight, are able to synthesize sugar from the simple substances carbon dioxide and water: but man has not yet discovered how to do it cheaply and in large quantities. He may one day discover a catalyst (this will be explained later) which will help him to do it.

Indeed, the subject of catalysis, which is explained in a later chapter, is likely to become of increasing importance. Here is an example from the World War of

1914–18. Almost at its close — too late, in fact, for the substance to be used in it — the Americans discovered a deadly "gas" which they called Lewisite (after the inventor). The first consignment was shipped to Europe at the end of October, 1918, and was still on its way when the Armistice was signed. It was therefore destroyed at sea. It was made by the action of the well-known gas acetylene on a compound known as arsenic trichloride. This action, no doubt, would have taken place very slowly in any case. But it was caused to go on in the presence of aluminium trichloride, which remained aluminium trichloride at the end, and served merely to speed up the reaction very greatly. Substances which act in this way, i.e. which accelerate or retard chemical actions, themselves remaining unchanged at the end, are known as catalysts.

Catalysts are often discovered accidentally. You have just been reading that indigo is manufactured from naphthalene as the starting-point. The first part of the process consisted in converting naphthalene into something else, using sulphuric acid. The process was very slow, and the yield was poor. But one day the chemists withdrew a sample of the mixture from the vat, in order to analyse it and see how far the reaction had gone. This was their normal procedure, and they expected that in that short time very little of the naphthalene would have been converted. To their astonishment, the reaction was very nearly complete. They investigated, and found that a thermometer which had been immersed in the mixture had broken. The mercury had escaped into the mixture, and had been converted into mercury sulphate by the sulphuric acid. After that, they always added a little mercury sulphate as a catalyst, and thus the accident was largely responsible for the success of the process.

Chemistry has given rise to quite new industries, e.g. the manufacture of "plastics"; the discovery of new plastics is becoming of ever-increasing importance.

"Bakelite" is a well-known plastic. So is the substitute for glass — perfectly transparent, but without the brittleness and splintering properties of glass — used in aircraft. Think of the articles already made of these substances — fountain-pen holders (other than vulcanite or metal), switch-covers, barrels of electric torches, containers, screw caps for bottles, and a hundred other things. Plastics are cheap and easily moulded, and may in time replace cans for food-stuffs. It is all a matter for further research, for the life of a manufacturing concern is in its research laboratory.

At one time it was believed that the substances formed within the bodies of plants and animals (that is, in organisms) could not be obtained from any other sources. There are thousands of them, and they are all substances containing carbon. Since they occur in organisms, the study of them was called *organic* chemistry. The study of substances occurring otherwise was called *inorganic* chemistry. The gap between these two branches of chemistry was bridged in 1828 by the German chemist Wöhler, when he synthesized the substance urea (a well-known substance produced by the bodies of animals, including man) from purely inorganic materials and without the use of organisms. For convenience, the science is still divided into organic and inorganic chemistry. The former is the chemistry of the carbon compounds (though a few of these are included in inorganic chemistry, as you will see in the chapter on carbon). If you go on from the stage reached in this book to do more advanced chemistry, you will begin on organic chemistry, which is even more fascinating than inorganic chemistry.

But you must first know the general principles of chemistry and the use of the "tools" employed in it. This is the reason why inorganic chemistry is always studied first.

Before we begin on it, let this chapter conclude as it began. It is to be hoped that you will not study chemistry

for its bread-and-butter value alone: that you will not regard it merely as a subject at which to work in order that you may have a better chance of getting a School Certificate: that, if you do not intend to take up chemistry in after-life, or pharmaceutical chemistry, or medicine, or dentistry, or engineering, you will still value the subject for its own sake as a factor in the *training* of your mind. If it is properly studied, and the *spirit* of the study is right, it will satisfy many of your intellectual demands, give you a more valuable outlook on life, a respect for the fearless pursuit of truth, a reverence for the men who gave their lives to this pursuit, and a lively interest in everything around you.

CHAPTER II

PHYSICAL AND CHEMICAL CHANGE: MIXTURES AND SINGLE SUBSTANCES: ELEMENTS AND COMPOUNDS

PHYSICAL AND CHEMICAL CHANGE

In chemistry we are concerned with certain changes which matter undergoes. Matter, as you have probably already learnt, is anything that we can see or feel or smell; it is anything that has weight.

There are innumerable changes which everyone has observed: things are warmer in summer than in winter; a ball thrown upwards changes its motion, getting slower until it finally stops, and then begins to descend; water when cooled changes to ice, and when heated changes to steam.

In these changes that we have mentioned, however, we are concerned with substances which contain the same kind of matter after the change as they contained before. The things that are warmer in summer than in winter are still made of the same kind of matter; the ball is still the same ball in every respect when it is descending as when it was going up; ice and steam (not quite so obviously) are still made up of the same kind of matter as the liquid water from which they came.

Also, these changes can be made to go backwards; we say that they are *reversible*. Ice and steam can be warmed and cooled respectively to get water in the same form as we started with; things made hotter can be cooled and are the same as before.

These are examples of what is known as *physical change*.

In a physical change no new kind of matter is formed, and the change is usually quite easily reversible.

The changes with which we are chiefly concerned in chemistry are of a different kind. Some examples with which you are familiar are: A match when struck changes from a piece of wood with a small lump of brown matter on one end to a shrivelled, lighter, brittle piece of charcoal. Coal when heated in a retort in a gas works changes from a shiny black solid to several substances: coke, tar, ammonia, and the gas we use in houses for cooking. A bright iron nail, when left in moist air or water for some time, changes on the surface to a reddish-brown powder called rust.

Here, obviously, is a class of change different from that previously discussed. We no longer have the same substance as we had before: the charcoal is different from the match; the products formed when coal is heated are different from the coal; rust is different from iron. Moreover, these changes are not reversible.

In a chemical change a new substance or substances are formed, the process is not generally reversible, and heat is generally given out. (Heat is sometimes taken in.)

Try the following changes and note whether it is obvious that a new substance is formed or not, and whether you can detect any heat given out, and whether the change is reversible or not. Say in each case whether it is a physical change or a chemical change.

(i) Hold a couple of inches of magnesium ribbon in a pair of crucible tongs, and place the end in a Bunsen flame until a change begins.

(ii) Add a few drops of silver nitrate solution to a little sodium chloride (common salt) solution in a test-tube.

(iii) Place the test-tube and contents left after (ii) in sunlight or bright daylight, and leave it for several minutes.

(iv) Add a few drops of potassium bromide solution to a little lead nitrate solution in a test-tube.

(v) Heat the contents of the test-tube after (iv) until no further change is noticed, and then let it cool.

(vi) Measure the diameter of a penny with calipers. Hold it with crucible tongs in a Bunsen flame until it is red hot, and measure it again. Let it cool to room temperature and measure its diameter once more. Notice any change on the surface of the coin. (The penny can be cleaned and used for its proper purpose afterwards.)

(vii) Place a few crystals of ammonium dichromate in a test-tube. Warm gently over a Bunsen flame until a change begins.

MIXTURES AND SINGLE SUBSTANCES

In chemistry we divide all matter into two classes: *mixtures* and *single substances*, or *pure substances.*

Let us consider something that you know to be a mixture, say, for example, a mixture of common salt and sand, which you can easily make up and examine for yourself. If you look at it closely you can see the individual particles of salt and those of sand. If you had sufficient patience you could effect a separation of the two by picking them out by hand. You could separate them much more effectively by dissolving out the salt with water, pouring off and evaporating the solution, and drying the salt. Neither of these methods of separation involves chemical change. If you were to measure the density of the mixture and compare the result with that obtained in the case of another mixture of salt and sand, the two answers would be different: the salt and the sand may be in any proportions. The mixture still has the sharp taste of salt and the grittiness of sand.

Now let us consider a single substance. Common salt itself is a single substance. Chemists have found out that although common salt—or sodium chloride, to give it its chemical name—is really made up of two other well-known single substances, sodium and chlorine, it is itself a single substance. If you have ever seen any

sodium you will have observed that it is a metallic-looking substance, and you may know that chlorine is a gas. Obviously the particles of these two constituents cannot be seen in the salt. Each particle of salt looks like every other particle. You cannot separate common salt into sodium and chlorine by any such mechanical method as can be employed in the case of a mixture; in order to do so it is necessary to supply energy (usually in the form of electricity) and effect a chemical change.

Again, common salt has none of the properties of sodium and none of chlorine. If you were unwise enough to place some sodium on your tongue you would hear a hissing noise or a bang, great heat would be given off, a gas would be evolved, and a substance (caustic soda) would be formed, which would burn into your tongue. Chlorine was used as a poison gas during the 1914–18 war. Yet every day you pile some common salt, made up of nothing but these two dangerous substances, on your plate and consume it with your food. Obviously, then, salt has none of the properties of the constituent substances which make it up, but has a set of properties entirely its own.

Another important point about single substances is that they have each a definite set of properties. Every grain of salt, no matter where it comes from (provided it contains no impurity) is a colourless crystalline substance having a density of 2·17 gm. per cubic centimetre, and dissolving to the extent of 35·8 gm. of salt per 100 c.c. of water at 10° C., and it contains exactly 39·3 per cent of sodium and 60·7 per cent of chlorine by weight.

Copper is another example of a single substance. Its particles are all the same; it is made up of nothing but copper, and so the question of separation does not arise; it has a definite set of properties — you cannot get a sample of pure copper denser than any other sample, or with a different melting-point, or with different chemical properties.

A mixture contains particles of different kinds; it can generally be separated into its constituent substances mechanically; its properties are the average properties of its constituents.

A single substance contains particles of only one kind; it has a definite set of properties; if composed of two or more single substances combined, it contains them in definite proportions by weight, and has a special set of properties of its own different from those of the substances composing it; it cannot be separated mechanically into its constituents.

ELEMENTS AND COMPOUNDS

A single substance which cannot be divided into anything simpler is called an element. There are 92 known elements, and everything which exists on earth is made up of one or more of these. Of course it may some day be found that a substance which we now regard as an element can be split up into two simpler substances. This " element " would then be called a *compound*, and the newly-discovered substances would be elements. For reasons which are beyond the scope of this book, however, it is unlikely that such a discovery will be made.

A single substance that can be split up into two or more elements is called a *compound*.

Some of the commonly-occurring elements of which you may have heard are:

Aluminium Al	Gold	Magnesium Mg	Oxygen O	Sodium
Calcium Ca	Hydrogen H	Manganese Mn	Platinum	Sulphur
Carbon C	Iodine I	Mercury Hg	Potassium K	Tin
Chlorine Cl	Iron F	Nickel Ni	Silicon Si	Zinc
Copper Cu	Lead Pb	Nitrogen N_2	Silver Ag	

On p. 14 are listed a few of the million and more chemical compounds known, with their chemical names and the names of the elements of which they are composed.

Notice that the chemical name is in most cases derived from the names of the elements contained in the compound.

Everyday Name	Chemical Name	Elements Contained
Alcohol ..	Ethyl alcohol.	Carbon, hydrogen, oxygen.
Chalk ..	Calcium carbonate.	Calcium, carbon, oxygen
Common salt	Sodium chloride	Sodium, chlorine.
Epsom salt ..	Magnesium sulphate.	Magnesium, sulphur, oxygen
Saltpetre ..	Potassium nitrate.	Potassium, nitrogen, oxygen
Sulphuric acid	Sulphuric acid	Hydrogen, sulphur, oxygen.
Sugar ..	Sucrose.	Carbon, hydrogen, oxygen.
Water ..	Hydrogen oxide.	Hydrogen, oxygen.

Notice also that both alcohol and sugar are composed of the same three elements combined together. There are thousands of different compounds made up of carbon, hydrogen, and oxygen, each compound containing the three elements in definite proportions, but different from their proportions in every other such compound. But do not think that you can add a little more carbon and a little more hydrogen to sugar and produce alcohol. Certain chemical changes are necessary, as the alcohol, like the sugar, is a compound and not a mixture.

Some mixtures with which you are well acquainted are:

Mixture	Single Substances Contained
Brass ..	Copper, zinc.
Ink	Ferrous tannate, gum, indigo, sulphuric acid, water.
Milk ..	Water, a sugar, fats.
Paper ..	Cellulose, alum, china clay, etc.
The Air ..	Nitrogen, oxygen, carbon dioxide, water vapour, other gases.

SOME METHODS FOR SEPARATING MIXTURES

(*a*) A soluble and an insoluble solid

Let us take as an example a mixture of common salt and sand.

Place the mixture in a beaker and add water until the level is twice as high as that of the mixture. Place the beaker and contents on wire gauze on a tripod and heat gently, stirring with a glass rod (fig. 1). After a few minutes, when the mixture is fairly hot, pour the clear liquid down the glass rod into a filter paper in a funnel which is resting in the neck of the flask. When the liquid

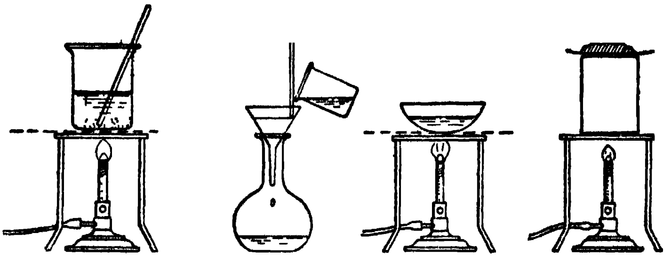


Fig. 1. — Separation of Salt and Sand

has nearly all gone from the beaker, stir it up and pour the wet sand into the filter, if necessary washing out the beaker with a little more clean water. When the liquid no longer runs out of the funnel, pour it into an evaporating basin and evaporate to dryness, heating very carefully at the end to avoid spluttering. Examine the white residue. Taste it. It is salt without any trace of sand in it.

While the evaporation is proceeding, wash the sand on the filter paper by three times filling it up with pure water and letting it drain out. Then carefully extract the filter paper from the funnel and spread it out on an upturned tin, such as a treacle tin, and warm the air in the tin with a *small* Bunsen flame. Care must be taken

not to have the tin so hot that the paper chars. Soon the sand will be dry. Look if you can see any salt in it. Place a little on your tongue and notice if any salt can be tasted. It is sand without any trace of salt in it.

(*b*) Two soluble solids

Two methods may be mentioned here, but you will not be required to carry them out yourself. They are **fractional crystallization** and **sublimation.**

Fractional crystallization takes advantage of the fact that although each of the substances is soluble in water, the solubility of one is sure to differ from that of the other. So when a solution is made and evaporated, one will crystallize first. The process has to be repeated several times to effect a good separation, and it is laborious and needs very great care.

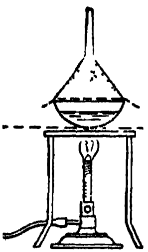


Fig 2.—Sublimation

Sublimation is a good method with certain substances. It is employed where one of the constituents of the mixture *sublimes*, that is, changes directly from solid to vapour on heating, without going through the liquid stage. The two substances with this property that you are likely to come across are ammonium chloride (sal ammoniac) and iodine. A mixture of, say, common salt and sal ammoniac is placed in an evaporating basin, a piece of filter paper (perforated by pushing a piece of glass rod through it a number of times) is placed over the basin, and a filter funnel is inverted over it. On heating, the sal ammoniac will sublime and the vapour will turn again to solid on the top of the perforated filter paper and on the cool sides of the funnel. The salt will, of course, remain in the basin (fig. 2).

(*c*) Magnetic separation

This is used in industry. The powdered mixture is allowed to fall between the poles of a powerful magnet, and any magnetic substances are deflected, so that they and the non-magnetic substances fall into two heaps.

(*d*) Sedimentation

This is generally used for separating metallic ores from rock, as, for example, in the washing of gold. The crushed material is submitted to a stream of water. The rock particles are washed away and the denser particles of metal, or metallic ore, sink.

Winnowing is another example of this principle used in practice. A lighter powder can be separated from a heavier one by blowing air over the mixture.

(*e*) Separation of two immiscible liquids

A *separating funnel* is used for this purpose. A mixture of, say, oil and water is poured into a separating funnel held vertically in a clamp (fig. 3). The surface between the two liquids can readily be seen. The denser water is allowed to run out of the funnel by opening the tap until it has nearly all gone through. The remainder and the first few drops of the lighter oil are generally allowed to run to waste, and then the lighter liquid is run off into another vessel. It is not possible to effect a perfect separation by this method, as generally a little of each liquid will dissolve in the other: the water will contain a small quantity of oil dissolved in it, and the oil will contain a little dissolved water.

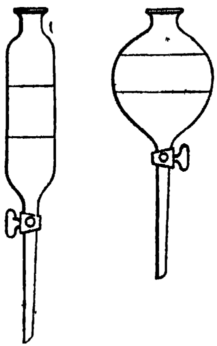


Fig. 3.—Separating Funnels

(*f*) Separation of two miscible liquids (*fractional distillation*)

The mixture is heated in a flask and the constituent liquids will boil at different temperatures. Their vapours are made to condense, and the liquids are collected separately. A **Liebig's condenser** is generally used (fig. 4). It consists of a central tube leading from the flask to the receiving vessel. This tube is surrounded by

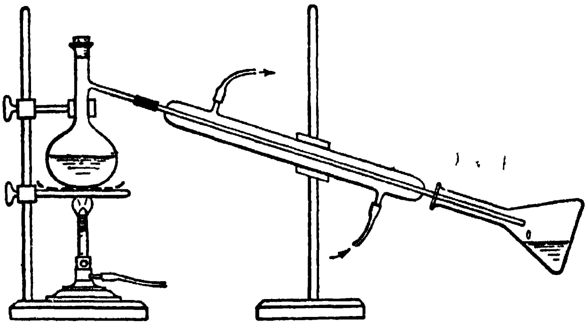


Fig. 4. — Distillation

a glass jacket through which cold water is circulated. Commercially much more elaborate constructions are used. Petroleum is separated in this way into a large number of fractions, producing oils useful for different purposes, from aviation spirit (boiling-point 40° C to 70° C.) to fuel oil (boiling-point 250° C. to 350° C.)

QUESTIONS

1. What do you understand by *physical change* and *chemical change*? Describe three physical changes and three chemical changes with which you are familiar, and say why you consider each change to be physical or chemical.

2. Say whether each of the following is a chemical change or a physical change. Give your reasons.

(*a*) Salt gets wet when exposed to moist air.

(*b*) Iron rusts when exposed to moist air.

(*c*) Sugar dissolves in water.

(*d*) " Health salt " dissolves in water.

(*e*) Spring cabbage grow rapidly when the ground is treated with nitrate of soda.

(*f*) When an egg is boiled the yolk and white go firm.

3. What are the differences between a mixture and a single substance?

Give three reasons for supposing air to be a mixture and three for supposing water to be a single substance.

4. How would you obtain samples of pure salt and pure chalk from a mixture of the two?

5. How would you separate a mixture of salt, sand, and sal ammoniac into its constituent parts?

6. Describe a separating funnel and a Liebig's condenser, and explain the use of each.

7. Explain the difference between an element and a compound.

CHAPTER III

BOYLE'S LAW AND CHARLES' LAW

There are two gas laws of great importance to the chemical worker; they are known as **Boyle's Law** and **Charles' Law.**

You will come across many quantitative experiments in chemistry where the result depends upon the volume of a gas collected in a measuring tube. Now, suppose you did such an experiment on Monday when the weather was cold and crisp, i.e. when the air temperature was low and the air pressure was high. You would collect, let us say, 53 c.c. of gas. But if you had done this experiment on Wednesday instead of Monday, when the weather was close and warm, i.e. when the air temperature was higher and the air pressure lower, you would have found that the volume of gas collected was considerably greater, perhaps 56 c.c.; this even though the conditions and quantities taken in the experiment were precisely the same as before, the only difference being the different weather conditions.

When a chemist working in industry does an experiment of this type, his small laboratory quantities are a sample of perhaps many tons of materials used in his industrial works, and so a small change in atmospheric conditions means a very large difference in whatever the sample represents.

There are two causes of this change in the volume of a gas: one is pressure, the other temperature. Let us take them separately.

Effect of pressure on the volume of a gas

If you pull out the handle of a cycle pump, place your finger over the hole at the other end, and then push the handle in, you find that as you increase the pressure on the trapped air the volume diminishes. Or you might say that as you decrease the volume of the gas, the pressure increases — you can feel it pressing back with increasing force as the volume is diminished. That is, the greater the pressure the smaller the volume, and the smaller the pressure the greater the volume. Even the small change in the pressure on a gas due to a change of weather conditions causes an appreciable difference in its volume. This relation between pressure and volume of a gas is summed up in a law discovered by *Robert Boyle* in 1662.

Boyle's Law

At constant temperature the volume of a gas varies inversely as the pressure on it.

That is, if the pressure is doubled the volume is halved; if the pressure is only a third of what it was before, the volume is three times the original volume. When two quantities vary in this way, i.e. *inversely*, their product is constant. We can therefore represent the law by

$$P \times V = \text{constant, or } P_1V_1 = P_2V_2,$$

where P_1 and V_1 are the pressure and the volume respectively under certain conditions, and P_2 and V_2 those under new conditions.

EXAMPLE. — A gas is found to have a volume of 57·5 c.c. when the pressure is 74·4 cm. of mercury. What will the volume be when the pressure is 76 cm.?

$$P_1V_1 = P_2V_2,$$

$$\text{i.e. } 74{\cdot}4 \times 57{\cdot}5 = 76V_2.$$

$$V_2 = \frac{74{\cdot}4 \times 57{\cdot}5}{76} \text{ c.c.}$$

$$= 56{\cdot}4 \text{ c.c.}$$

The pressure 76 cm. of mercury is called *standard pressure*, and we always express the volume of a gas as the volume it would occupy under standard pressure.

Effect of temperature on the volume of a gas

You doubtless know that it is a general rule that when a substance is heated it expands and when it is cooled it contracts. This expansion and contraction is different for different solids and liquids, but it is found that *all* gases expand and contract to the same extent under the same changes of temperature. The coefficient of expansion of all gases is $\frac{1}{273}$. This fact is embodied in what is known as *Charles' Law.*

Charles' Law

All gases expand by $\frac{1}{273}$ of their volume at 0° C. for each degree C. rise of temperature, provided they are maintained at constant pressure.

That is, if V_t is the volume at t° C. and V_0 is the volume at 0° C.,

$$V_t = V_0 + \frac{t}{273}V_0,$$

$$\text{i.e. } V_t = V_0\left(1 + \frac{t}{273}\right),$$

$$\text{or } V_t = V_0\left(\frac{t + 273}{273}\right).$$

To make the calculation quicker, and for other reasons, we set up a new scale of temperature, called the *Absolute Scale*, in which the temperature is the Centigrade temperature + 273, i.e. $t + 273$. E.g. 0° C. = 273° A., 10° C. = 283° A., − 10° C. = 263° A., and −273° C. = 0° A.

Our last equation above now becomes

$$V_t = \frac{V_0 T}{273},$$

where T is the temperature on the absolute scale.

The volume at 0° C., i.e. V_0, is constant for a given mass of gas, and 273 is, of course, a constant, and so $V_t =$ a constant $\times T$, or V_t is proportional to T. Charles' law may then be expressed:

For a given mass of gas at constant pressure the volume varies directly as the absolute temperature.

When two quantities vary directly, the quotient of one divided by the other is constant, and so we may write Charles' law as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}.$$

EXAMPLE. — A gas has a volume of 75·5 c.c. when the temperature is 15° C. What will be the volume when the temperature is 0° C., the pressure remaining constant?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2},$$

(Remember that T_1 and T_2 are in absolute units.)

$$\text{i.e.} \quad \frac{75{\cdot}5}{288} = \frac{V_2}{273}.$$

$$\therefore \quad V_2 = \frac{75{\cdot}5 \times 273}{288} \text{ c.c.}$$

$$= 71{\cdot}6 \text{ c.c.}$$

0° C., i.e. 273° A., is called *standard temperature*, and we always express the volume of a gas as the volume it would occupy at standard temperature.

The Gas Equation

We now have two laws, Boyle's and Charles', by which we can, if we have a certain volume of gas collected under any conditions of temperature and pressure, calculate what volume it would occupy under standard conditions of temperature and pressure, i.e. 0° C. and 76 cm. Standard Temperature and Pressure is generally

written S.T.P., sometimes N.T.P. (Normal Temperture and Pressure).

Boyle's law says that when the temperature is constant the volume varies inversely as the pressure.

Charles' law says that when the pressure is constant the volume varies directly as the absolute temperature.

It is convenient to combine these two laws, which can then be stated as follows:

When both the temperature and the pressure of a gas are changed, the volume varies inversely as the pressure and directly as the absolute temperature.

It may be written as

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}.$$

EXAMPLE. — In an experiment a gas was collected and found to have a volume of 63·7 c.c. The temperature of the laboratory was 15·5° C., and the atmospheric pressure was 74·7 cm. What volume would the gas occupy at S.T.P.?

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2},$$

$$\text{i.e.} \quad \frac{74\cdot7 \times 63\cdot7}{288\cdot5} = \frac{76 V_2}{273}$$

$$V_2 = \frac{74\cdot7 \times 63\cdot7 \times 273}{288\cdot5 \times 76} \text{ c.c.}$$

$$= 59\cdot23 \text{ c.c.}$$

QUESTIONS

1. State Boyle's law and Charles' law. Why are they important in chemistry?

2. What is meant by (*a*) Absolute scale of temperature, (*b*) Standard Temperature and Pressure?

3. A gas has a volume of 55·0 c.c. when the pressure is 774 mm. What will be its volume at 760 mm. pressure, the temperature remaining the same?

4. A gas has a volume of 74·6 c.c. when the pressure is 749 mm. What pressure will be necessary to compress the gas to 50 c.c., the temperature remaining constant?

5. When the temperature is 12° C. a gas has a volume of 50·0 c.c. What will be its volume when the temperature is 20° C., the pressure being unchanged?

6. A gas has a volume of 47·3 c.c. when the temperature is 15° C. If the pressure is kept constant, at what temperature will the gas have a volume of 100 c.c.?

7. In an experiment a gas collected is found to have a volume of 39·4 c.c. The air temperature is 13° C. and the barometer reads 742 mm. Calculate the volume of the gas at S.T.P. $\frac{V_1P_1}{T_1} = \frac{V_2P_2}{T_2} = \frac{39.4 \times 742}{273+13} = \frac{760V_2}{273}$

8. A gas has a volume of 55 c.c. when the temperature is 10·5° C. and the pressure is 774 mm. If the temperature rises to 15° C., what pressure will be needed to compress the gas to 40 c.c.? $\frac{P_1V_1}{T_1} = \frac{V_2P_2}{T_2} = \frac{774 \times 55}{283.5} = \frac{40V_2}{273+15}$

9. A gas measures 48·5 c.c. at S.T.P. When the pressure is 743 mm. the gas is found to have a volume of 60 c.c. What is then the temperature?

742 × 60 =

CHAPTER IV

THREE QUANTITATIVE CHEMICAL LAWS

The Atomic Theory, which we shall soon be discussing, is a reasonable explanation of the way in which matter is made up, and the way in which chemical substances change. It is based upon definite facts that are well known and can at any time be verified in the laboratory. These facts are expressed in what are known as *laws*.

A law is a general statement that expresses a number of different but connected facts. We can now examine three laws that will help us to understand the atomic theory.

The law of conservation of matter

Matter cannot be created or destroyed in any chemical change.

This means that never has any scientist found, if he were able to make accurate measurements, that he finished up with the slightest amount more or the slightest amount less matter than he started with. This is not always obvious. When a candle burns it may seem that matter is destroyed, but if the total weight of the candle and the air used up in its burning is compared with the total weight of the solids, liquids, and gases formed by the burning, the two totals are found to be exactly the same.

i.e. Weight of part of candle used + Weight of part of air used

= Weight of soot, etc., formed + Weight of water vapour formed + Weight of gases formed.

Experimental verification of the law of conservation of matter. — (This is most conveniently done in cases where liquids and solids are used and formed. Where gases are concerned it is a little more difficult, but it can be done nevertheless.)

Take two liquids A and B which you know to react chemically with one another (see Chapter II, p. 10), and put one in a small test-tube and the other in a conical flask (fig. 5). Place the test-tube in the flask, keeping it upright with a piece of cotton. Fit the flask tightly with a rubber stopper. Weigh the flask and contents. Now tilt the flask and allow A and B to mix. You will notice that a chemical change takes place. After the change is complete, let the flask and contents cool, and weigh again.

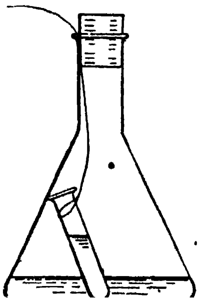


Fig. 5. — Experimental Verification of the Law of Conservation of Matter

You will find that there is no change in weight whatever.

i.e. Wt. of flask, etc. + wt. of A + wt. of B
= Wt. of flask, etc. + wt. of new substances formed.

∴ Wt. of A + wt. of B
= Total weight of new substances formed.

Substances A and B which can conveniently be used for this experiment, together with the names of the new substances formed, are:

(1) Silver nitrate (solution) + sodium chloride (solution)
→ silver chloride (insoluble solid) + sodium nitrate (solution).

(2) Barium chloride (solution) + sulphuric acid (solution)
→ barium sulphate (insoluble solid) + hydrochloric acid (solution).

(3) Lead nitrate (solution) + potassium bromide (solution)

→ lead bromide (insoluble solid) + potassium nitrate (solution).

(4) Copper sulphate (solution) + sodium hydroxide (solution)

→ copper hydroxide (insoluble solid) + sodium sulphate (solution).

(5) Bright iron nail (solid) + tap water (liquid)

→ rust (solid) + unchanged iron + unchanged tap water.

No. 5 should be left for a week between weighings, and the test-tube can be dispensed with. (It is chiefly the air dissolved in the tap water that causes the rusting. See p 260.)

The law of constant composition (also called the law of definite proportions)

In any chemical compound the elements are combined together in definite proportions by weight.

If you were to analyse accurately some sodium chloride, you would find that every hundred parts by weight of the salt was made up of 39·3 parts of sodium and 60·7 parts of chlorine. You could not possibly get salt containing a little more sodium or a little more chlorine than any other sample of salt. The same result would be obtained no matter what the source of the salt, provided that you started with a pure sample. It could be from a Cheshire salt mine, from the Dead Sea, or made in the laboratory from hydrochloric acid and sodium hydroxide, or by burning sodium in chlorine gas.

Experimental verification of the law of constant composition. — We may analyse three samples of black copper oxide obtained by different methods.

(*a*) Heat a little copper carbonate in a crucible for some time and allow the black powder formed to cool in a desiccator. Call this copper oxide Sample A.

(*b*) Add concentrated nitric acid carefully to a few small pieces of copper in a crucible placed in a fume cupboard. When no more brown fumes are given off on adding a drop more of the acid, evaporate the green substance to dryness and heat the solid (copper nitrate) until no more fumes are evolved and a black solid (again copper oxide) is left. Let this cool in a desiccator, and call it Sample B.

(*c*) Take a sample of *pure* copper oxide from the bottle, heat it strongly, and put it with the other samples in a desiccator, and call it Sample C.

Three porcelain boats are needed to hold the three

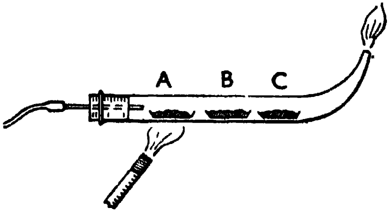


Fig. 6. — Verification of the Law of Constant Composition

samples of copper oxide. These should be heated in a stream of coal gas in a hard glass tube, the gas being burned at the upturned jet (fig. 6). After a while they should be allowed to cool a little where they are, and then finish cooling in the desiccator. When cool, each boat is weighed, a sample of copper oxide is placed in each, and the boat is weighed again.

The three boats are now introduced carefully into the hard glass tube; coal gas is passed over (burnt as before on leaving the tube) and the boats are heated from below by means of a Bunsen burner held in the hand. Each boat is heated for a minute after a glow is noticed and a brown powder of copper is formed. The boats are allowed to cool with the gas still passing over, and then weighed again.

Tabulate your results as follows:

	Sample A	Sample B	Sample C
Wt. of boat empty	7·49 gm.		
Wt. of boat + copper oxide	10·15 gm.		
Wt. of boat + copper ..	9·61 gm.		

CALCULATION:

Sample A.

Weight of copper oxide = 2·66 gm.

Weight of copper = 2·12 gm.

$$\left.\begin{array}{r}\text{Percentage of copper}\\ \text{in the copper oxide}\end{array}\right\} = \frac{2{\cdot}12 \times 100}{2{\cdot}66} = 79{\cdot}7 \text{ per cent.}$$

Repeat the calculation for samples B and C. You should get the three answers approximately the same, namely, about 80 per cent of the copper oxide is copper.

If every precaution were taken to ensure absolute purity of substance and accuracy of measurement the results would be identical, and so we should see that in each sample of copper oxide, no matter what its origin, the elements copper and oxygen are combined together in definite proportions by weight.

This, then, illustrates the law of constant composition.

The law of multiple proportions

If two elements combine together in more than one way to form more than one compound, then the weights of one which, separately, combine with a fixed weight of the other, are in a simple ratio.

You may not grasp the meaning of this law immediately, as it is difficult to express it simply in a few words. However, read it carefully several times and when you have understood its meaning learn it by heart; you may find it difficult to express clearly in your own words in the heat of an examination.

This will help you to see its meaning: copper, as you

may have noticed from the bottles on the shelves, ~~forms~~ *two* oxides, one black and one red. Now, if you were to analyse each by the method used in the last experiment and work out in each case how much oxygen combines with a fixed weight — say 1 gm. — of copper, you would find that the weight of oxygen in the case of the black oxide is *exactly twice* that of the oxygen in the red oxide.

That is, in the wording of the law of multiple proportions, the weights of oxygen which, separately, combine with a fixed weight of copper are in the ratio of 2 : 1.

Verification of the law of multiple proportions. — We may use these two oxides to verify this law.

Weigh two porcelain boats and then weigh each again with some of the black oxide in one and some of the red oxide in the other. Place the boats in a hard glass tube and heat in an atmosphere of coal gas as in the previous experiment. Allow them to cool with the gas still passing over, and weigh again.

Tabulate your observations as follows:

	Black Oxide	Red Oxide
Weight of porcelain boat empty	7·49 gm.	8·26 gm.
Weight of boat + copper oxide . .	9·62 gm.	12·12 gm.
Weight of boat + copper	9·19 gm.	11·69 gm.

CALCULATION:

Black oxide.

Weight of black oxide $= 2{\cdot}13$ gm

Weight of copper in oxide $= 1{\cdot}70$ gm.

$\therefore$ Weight of oxygen in oxide $= 0{\cdot}43$ gm.

i.e. 1·70 gm. of copper combine with 0·43 gm. of oxygen

$$\therefore \text{ 1 gm. of copper combines with } \frac{0{\cdot}43}{1{\cdot}70} \text{ gm. of oxygen}$$

$$= {\cdot}253 \text{ gm. of oxygen.}$$

Red oxide

Weight of red oxide $= 3{\cdot}86$ gm.

Weight of copper in oxide $= 3{\cdot}43$ gm.

$\therefore$ Weight of oxygen in oxide $= 0{\cdot}43$ gm.

i.e. 3 43 gm of copper combine with 0·43 gm. of oxygen.

$$\therefore 1 \text{ gm of copper combines with } \frac{0{\cdot}43}{3{\cdot}43} \text{ gm. of oxygen}$$
$$= {\cdot}125 \text{ gm. of oxygen.}$$

It is thus found that, within the limits of experimental error, the result in the first case is twice that in the second.

We very often find this ratio of 2 : 1, but it is not necessarily so. You will come across examples where the ratio is 2 : 3 or 3 : 4, and so on. Also you will find cases where two elements combine in more than two ways. Nitrogen and oxygen, for example, form no less than five different oxides of nitrogen, and it is found that the weights of oxygen which, in each case, combine with a fixed weight of nitrogen are in the simple ratio of 1 : 2 : 3 : 4 : 5.

Work out every example on this law, and you will thoroughly grasp its meaning. It is necessary to do so, as it is of very great importance in chemistry.

QUESTIONS

1. State the law of conservation of matter. How would you proceed to verify it in the laboratory?

2. State the law of constant composition. Explain how you would demonstrate its truth in the case of black copper oxide.

3. Three samples of water were found to have the following composition by weight:

(1) oxygen 12·72 gm., hydrogen 1·57 gm.;
(2) oxygen 22·25 gm., hydrogen 2·75 gm.;
(3) oxygen 9·89 gm., hydrogen 1·22 gm.

Show how these figures serve to verify the law of constant composition.

4. State the law of multiple proportions and describe an experiment to verify it.

5. Three oxides of nitrogen are found to have the following percentages by weight of oxygen: (i) 69·4 per cent, (ii) 53·3 per cent, (iii) 36·4 per cent.

Show that these figures verify the law of multiple proportions.

6. Two chlorides of chromium have the following composition by weight:

(i) chromium 42·31 per cent, chlorine 57·69 per cent.;
(ii) chromium 32·82 per cent, chlorine 67·18 per cent.

Show that these figures may be made to illustrate the law of multiple proportions.

7. Three oxides of lead contain 7·17, 9·34, and 13·37 per cent of lead respectively. Show that these figures are in agreement with the law of multiple proportions.

CHAPTER V

THE ATOMIC THEORY

In the history of chemistry there have been many vague theories to explain the nature of changes that matter is seen to undergo, and to explain the construction of matter itself. Some, due to the Greeks, closely resembled our present ideas as expressed in Dalton's atomic theory. But the theories of the ancient Greeks were never subjected to experimental test; they despised such work, and so a theory was supported or opposed without experimental evidence on either side.

Aristotle, one of the most famous of Greek philosophers, who died more than 300 years B.C., opposed the idea which had been put forward that matter was composed of minute indivisible particles (atoms), believing that all matter was made up of the four "elements": earth, air, fire, and water. His influence was so great that his ideas survived for many hundreds of years after his death.

We can say that, as a reasonable explanation of known and tested facts, the atomic theory was due to the schoolmaster-philosopher John Dalton (1766–1844). He had, of course, read of the ancient Greek theories, and he knew and had tested the law of conservation of matter. He discovered by careful experiment the law of constant composition. As a result he formulated his atomic theory. Then he went a stage farther, and deduced a new law — the law of multiple proportions — from his theory. Having deduced it theoretically, he proceeded to test it by experiment, and he found it to be true. This is rather unusual, for laws are generally made from a consider-

ation of known facts; in this case the law was deduced and found to be true afterwards.

The atomic theory can be summarized as follows:

(i) All matter is composed of minute indivisible particles called **atoms**. These atoms cannot be created or destroyed.

(ii) All atoms of any one element are identical in every respect, the most important respect being their weight.

(iii) The atoms of any one element are different (particularly in weight) from those of any other element.

(iv) When elements combine to form a compound, they do so by a union of atoms in simple small numbers. For example, one atom of element A will combine with one of B, or two of A with one of B, or two of A with three of B, and so on. These groups of atoms, forming a unit particle of a compound, are called **molecules**. Dalton called them " compound atoms ".

(v) All the molecules of any one compound are identical in every respect, and are different from the molecules of any other compound, even if that compound is composed of the same elements as the first.

It must be noted here that, although the term " molecule " is used to describe the smallest part of a compound formed by the union of atoms of different elements, the word is also used to describe the smallest part of any one element. This is because we find that elements generally exist as pairs of atoms, or with their atoms in groups of three or more. So two or more atoms of the *same* element will unite to form what is known as a molecule of that element. If an element exists in single atoms, and not in pairs, etc., then its molecule is the same as its atom.

We usually define atoms and molecules thus:

An atom is the smallest part of an element that can take part in chemical change.

A molecule is the smallest part of an element or compound that can exist separately.

Now let us see how the atomic theory as above ex-

pressed agrees with the three quantitative laws discussed in the last chapter.

1. The law of conservation of matter

Atoms being indivisible and indestructible, and chemical change being merely a regrouping of atoms, there can be no loss or gain of weight.

2. The law of constant composition

Consider a compound made up of elements A and B. According to the atomic theory, A and B have each a set of atoms, all A atoms being identical, and all B atoms being identical, and those of A different from those of B.

Suppose each A atom weighs x units, and each B atom weighs y units.

According to the atomic theory a simple small number of A atoms combine with a simple small number of B atoms to form the AB molecule. We will suppose 2 atoms of A unite with 3 of B. Then the weights of A atoms and B atoms combining to form one molecule of the AB compound are $2x$ and $3y$ respectively.

Now suppose ten million million molecules of the AB compound are formed. (This will form a small speck of the compound.) These will be made up of $2x$ weight-units of A and $3y$ weight-units of B for each molecule, and so the ratio of A to B by weight combining to form the compound will be

$$10{,}000{,}000 \times 2x : 10{,}000{,}000 \times 3y = 2x : 3y.$$

Similarly, if fifty million million molecules or any other number were formed, the ratio by weight of A to B combining to form the compound would be the same, namely $2x : 3y$.

As all molecules of any one compound are identical, no matter how the compound is prepared, or what its source, so long as it is the pure compound, its constituent elements will be in the same proportion by weight. This is the law of constant composition.

3. The law of multiple proportions

If A and B combine together in more than one way to form more than one compound, according to the atomic theory each different AB compound will contain a simple small ratio of A and B atoms, different from the ratio of the atoms in the other AB compounds.

For example, one may consist of 1 atom of A combined with 2 atoms of B, and the other of 2 atoms of A combined with 3 of B.

(As we shall see later, the formulæ of these compounds would be written AB_2 and A_2B_3 respectively.)

$\therefore$ two molecules of AB_2 would consist of 2 atoms of A and 4 atoms of B, and one molecule of A_2B_3 would consist of 2 atoms of A and 3 atoms of B.

The A atoms all weigh the same, and the B atoms all weigh the same;

$\therefore$ the weights of B which separately combine with the same weight of A (the weight of 2 atoms) are in the simple ratio of 4 : 3.

And multiplying several million million times as before, we get the same ratio. So the law of multiple proportions follows from the atomic theory.

QUESTIONS

1. State the law of conservation of matter, and show how it necessarily follows from the atomic theory.

2. What is meant by the terms *atom* and *molecule*? Explain how *atom* can only refer to elements, but *molecule* to both elements and compounds.

3. Write an account of the atomic theory. How does it explain the law of constant composition?

4. State the law of multiple proportions, and show how it must be true, assuming the atomic theory to be correct.

CHAPTER VI

EQUIVALENT WEIGHTS

The law of reciprocal proportions

This law was stated by Richter in 1792, some years before Dalton published his atomic theory. You will readily see that it is in agreement with the theory — in fact, it is to be expected if the theory is true. It may be expressed thus:

If an element combines with a number of other elements, the weights of those elements which separately combine with a fixed weight of the first are the weights in which they combine with one another, or simple multiples of those weights.

This law, like the law of multiple proportions, may seem somewhat complicated and difficult to understand at first, but it is really quite straightforward. Follow the example below, and then learn the law by heart.

Oxygen is found to combine with chlorine, hydrogen, and nitrogen to form chlorine monoxide, water, and nitrous oxide, respectively. The weights of these three elements which separately combine with the same weight (16 gm.) of oxygen are:

chlorine, 71 gm.; hydrogen, 2 gm.; nitrogen, 28 gm.

Now, chlorine combines with hydrogen to form hydrogen chloride, and the proportions of these two elements combining are found to be:

chlorine, 71 gm., with *hydrogen, 2 gm.*

Also, hydrogen combines with nitrogen to form ammonia, and the proportions are found to be:

hydrogen, 6 gm. ($= 3 \times 2$), with *nitrogen, 28 gm.*

Further, nitrogen combines with chlorine to form nitrogen trichloride, and the combining proportions of these elements are found to be:

nitrogen, 28 gm., with *chlorine, 213 gm.* (= *3* × *71*).

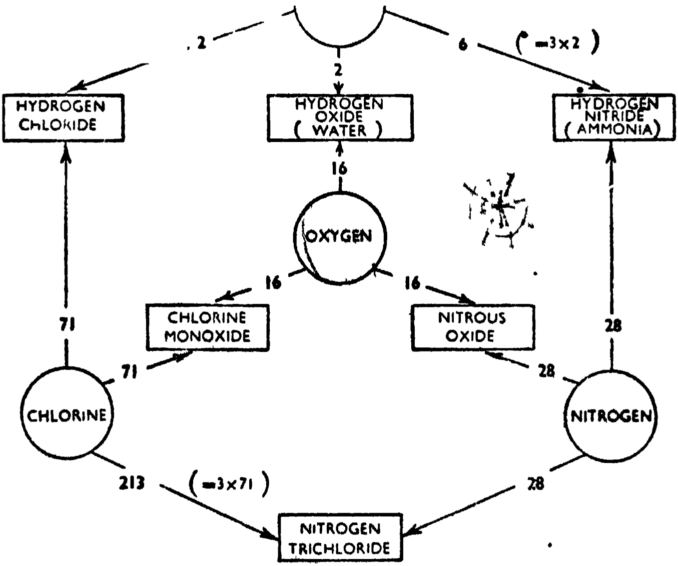


Fig. 7. — Combining Weights of Oxygen, Chlorine, Hydrogen, and Nitrogen

The above facts may be expressed in a diagram (fig. 7), the rings showing the four elements considered, and the rectangles showing the compounds formed. The numbers on the arrows indicate the proportions by weight in which the elements combine.

The law of reciprocal proportions applies not only to combination between two or more elements, but to every type of chemical change there is; the reacting weights

are definite and equivalent where compounds are concerned as well as elements.

For example, if some pieces of zinc are added to dilute sulphuric acid, the zinc is seen to dissolve and a gas, hydrogen, is given off. It is found that 32·5 gm. of zinc require 49 gm. of sulphuric acid (without the water, which does not change) to dissolve the zinc completely. If more acid than this is present, there will be some left over; if more zinc is added, 32·5 gm. of it will dissolve and the rest will be left over. The *weight* of hydrogen given off is found (by measuring the volume and calculating from the density) to be exactly 1 gm.

Other metals will turn out hydrogen from dilute sulphuric acid, and in each case 49 gm. of sulphuric acid will give 1 gm. of hydrogen, and a definite weight of the metal will be needed. For example, if magnesium is used, 12 gm. are required.

Moreover, if these weights of metals are dissolved in dilute hydrochloric acid instead of sulphuric acid, 1 gm. of hydrogen is evolved. The weight of hydrochloric acid used in each case is 36·5 gm.

Also 8 gm. of oxygen are found to combine with 32·5 gm. of zinc and 12 gm. of magnesium respectively.

Thus it may be said that 1 gm. of hydrogen is *equivalent* to 8 gm. of oxygen, and to 32·5 gm. of zinc, 12 gm. of magnesium, 49 gm. of sulphuric acid, and 36·5 gm. of hydrochloric acid.

This may be expressed by the diagram of fig. 8.

Definition of equivalent

The equivalent weight of an element or a compound is the weight of that element or compound that will combine with or displace or otherwise completely react with one part by weight of hydrogen, eight parts by weight of oxygen, or the equivalent weight of any other element or compound.

In the examples cited above the weights have all been given in grammes. This is merely for convenience; there is no unit for the equivalent weight of a substance.

The proportions are the same whether the substances are measured in ounces or tons. We often, however, have to express the equivalent weights in grammes, and this quantity is called the *gramme-equivalent* of the substance.

It is to be noted that as an element may combine with another element in more than one way, it may have

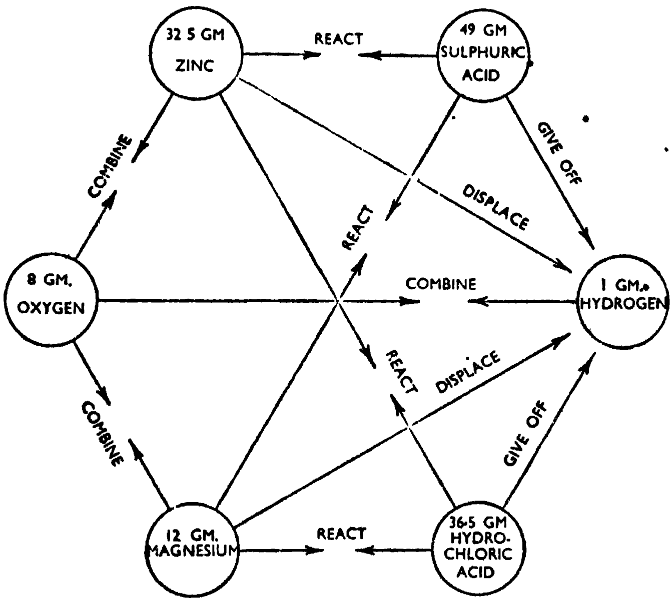


Fig. 8. — Equivalent Weights of Hydrogen, Oxygen, Zinc, Magnesium, Sulphuric Acid, and Hydrochloric Acid

more than one equivalent. The Law of Multiple Proportions says that when an element does so, the weights of it which separately combine with a fixed weight of the other are in a simple ratio, and so it follows that the different equivalents of an element are simple multiples of the smallest one. Thus copper forms two compounds with oxygen, in which 8 parts by weight of oxygen combine with 32 and 64 parts by weight of copper respec-

tively. The equivalents of copper are, then, 32 and 64 (= 2 × 32).

EQUIVALENT WEIGHTS OF COMPOUNDS

The equivalent weights of compounds were recognized first by Cavendish when, in 1766, he showed that the ratio of the weights of two acids which were needed to neutralize the same weight of one alkali was the same as the ratio of the weights of those acids which neutralized the same weight of another alkali. The question of equivalent weights of compounds, and particularly those of acids and bases, is very important for volumetric analysis, and you must understand it before being able to perform such analyses.

We know that hydrochloric acid consists of 35·5 parts by weight of chlorine combined with 1 part by weight of hydrogen. Hence the equivalent weight of hydrochloric acid is 36·5, as this weight contains 1 part by weight of hydrogen.

We also know that 40 parts by weight of sodium hydroxide contain 1 part by weight of hydrogen, so that the equivalent weight of sodium hydroxide is 40.

We also know by experiment that 36·5 gm. of hydrochloric acid exactly neutralize 40 gm. of sodium hydroxide.

Now if the equivalent weight in grammes of an acid is dissolved in a fixed volume, say 1 litre, of water, and the equivalent weight of an alkali is similarly dissolved in 1 litre of water, then 1 litre of the acid will just neutralize 1 litre of the alkali, and so any volume of the acid will just neutralize the same volume of the alkali. Solutions made up in such a way are called *standard solutions*, and the standard solutions generally used are *normal* or *decinormal* solutions.

A *Normal Solution* (N) contains the gramme-equivalent in 1 litre of solution.

A *Decinormal Solution* (N/10) contains one-tenth of the gramme-equivalent in 1 litre of solution.

It is clear that the strength of an alkaline (or acid) solution may be found by measuring how much of a standard solution of acid (or alkali) is needed to neutralize it.

METHODS OF DETERMINING EQUIVALENTS OF METALS

We may mention four methods by which equivalents of metals can be found experimentally.

METHOD 1. — This applies to a metal which dissolves in a dilute acid or alkali with the evolution of hydrogen,

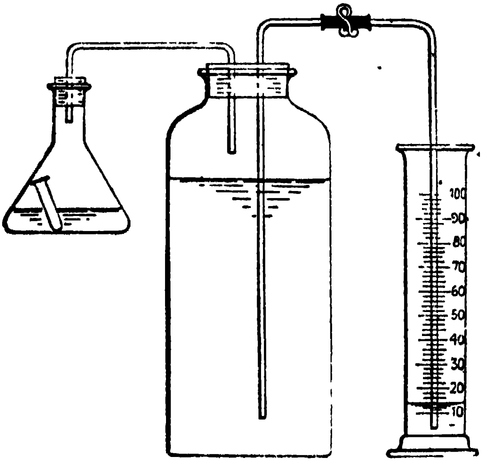


Fig. 9. — Equivalent of Metal by Displacement of Hydrogen

e.g. zinc, iron, magnesium, and calcium, all of which displace hydrogen from cold dilute sulphuric acid; and aluminium, which dissolves in hot dilute hydrochloric acid or hot sodium hydroxide solution.

About 1 gm. of the metal is weighed out accurately into a small test-tube. A conical flask contains the dilute acid or the sodium hydroxide solution (fig. 9). A delivery tube leads to a Winchester quart not quite full of water. Another delivery tube leads from beneath the

surface of this water to a measuring cylinder, via a pinch clip as shown. The apparatus is first tested to see that it is air-tight. The pinch clip is opened and a few cubic centimetres of water are seen to flow into the measuring cylinder and then stop, if there is no leakage. If water continues to drip, the stoppers must be seen to, and the apparatus tested again. When it is certain that the apparatus is air-tight, the volume of water in the cylinder is noted. The small test-tube is now allowed to fall, when the metal and acid will come into contact and hydrogen will be evolved. The gas goes into the Winchester and displaces its own volume of water into the measuring cylinder. Heat may have to be applied to the flask, as in the case of aluminium and dilute hydrochloric acid.

When the action has finished and the apparatus has cooled down to room temperature, the water levels in the bottle and cylinder are equalized by raising or lowering the cylinder, the pinch clip is closed, and the volume of water in the cylinder is measured. The volume previously there is subtracted, and this gives the volume of the hydrogen displaced from the acid by the metal. The temperature of the laboratory is now recorded, as is the pressure of the air, and the volume of gas obtained is corrected to S.T.P. The equivalent is calculated as follows

1·18 gm. of zinc, when dissolved in dilute sulphuric acid, displaced 424 c.c. of hydrogen. The atmospheric temperature and pressure were 12° C. and 753 mm. respectively.

$$\text{Volume of hydrogen at S.T.P.} = \frac{424 \times 753 \times 273}{760 \times 285} \text{ c.c.}$$
$$= 402{\cdot}4 \text{ c.c.}$$

But 1 c.c. of hydrogen is known to weigh 0·00009 gm.

$\therefore$ Weight of hydrogen $= 402{\cdot}4 \times {\cdot}00009 = {\cdot}03622$ gm.

i.e. ·03622 gm. hydrogen is displaced by 1·18 gm. zinc.

$\therefore$ 1 gm. hydrogen is displaced by $\frac{1{\cdot}18}{{\cdot}0362} = 32{\cdot}6$ gm. zinc.

i.e. Equivalent of zinc = 32·6.

METHOD 2. — In this method the equivalent is found by determining what weight of metal combines with 8 parts by weight of oxygen. It is particularly used in the case of copper, tin, and lead.

The metal is dissolved in nitric acid, which gives copper nitrate, tin oxide, and lead nitrate respectively. Where the nitrate is formed, heating decomposes it, forming the oxide. Details of the method are as follows:

Weigh out into a clean porcelain dish not more than 1 gm. of the metal, say copper. Add concentrated nitric acid drop by drop until the violent action stops and no more red fumes are evolved. Heat the residue, which consists of copper nitrate together with excess nitric acid, very gently until it is dry, and then more strongly. This drives off the spare nitric acid and decomposes the nitrate, leaving the oxide.

$$\text{Copper} + \text{nitric acid} \rightarrow \text{copper nitrate} \xrightarrow[\text{(heat)}]{} \text{copper oxide.}$$

Weigh the dish and contents when cool; this gives the weight of oxide formed.

The calculation is quite easy. The difference between the weights of oxide and metal is the weight of oxygen combined with the metal. A simple proportion sum will then give the weight of metal which combines with 8 gm. of oxygen. This is, of course, the equivalent of the metal, expressed in grammes.

The equivalent may also be found by the reverse of this process, i.e. by starting with the oxide. This method has already been described on p. 29, when we were demonstrating the truth of the Law of Constant Composition. Only one sample of oxide, of course, is used to find the equivalent of the metal. Let us take the observations given there.

Weight of boat empty	=	7·49 gm.
Weight of boat + copper oxide	=	10·15 gm.
Weight of boat + copper	=	9·61 gm.

From these figures 2·66 gm. of copper oxide contain 2·12 gm. of copper and therefore, by difference, 0·54 gm. of oxygen.

i.e. 0·54 gm. oxygen combine with 2·12 gm. copper.

$$\therefore\ 8 \text{ gm. oxygen combine with } \frac{2{\cdot}12 \times 8}{0{\cdot}54} \text{ gm. copper}$$

$$= 31{\cdot}4 \text{ gm. copper.}$$

i.e. Equivalent of copper = 31·4.

METHOD 3. — If the chloride of an element, i.e. a compound of that element with chlorine alone, is dissolved in water and a solution of silver nitrate is added, silver chloride is formed. This is insoluble in water and is therefore precipitated (i.e. formed as a solid which gradually settles at the bottom). If this is filtered off and dried and weighed, the weight of chlorine in the original chloride can be calculated, because we know that every 143·5 gm. of silver chloride contains 35·5 gm. of chlorine. Thus the weight of the element which combines with the equivalent (35·5) of chlorine can be calculated. This is, of course, the equivalent of the element.

Equivalent of potassium. — Weigh out accurately about 10 gm. of potassium chloride. Dissolve this in water and add excess of silver nitrate solution. A white precipitate is formed, which slowly turns grey. This is silver chloride. Filter and wash the precipitate with water, dry carefully, and weigh. Calculate your results as follows:

Weight of potassium chloride	= 10·10 gm.
Weight of silver chloride precipitated	= 19·41 gm.

The weight of chlorine in this silver chloride is $\frac{19{\cdot}41 \times 35{\cdot}5}{143{\cdot}5}$ gm.

$$= 4{\cdot}80 \text{ gm.}$$

i.e. 10·10 gm. of potassium chloride contain 4·80 gm. of chlorine, and hence 10·10 − 4·80 = 5·30 gm. of potassium,

i.e. 4·80 gm. chlorine combine with 5·30 gm. potassium.

$$\therefore\ 35{\cdot}5 \text{ gm. chlorine combine with } \frac{5{\cdot}30 \times 35{\cdot}5}{4{\cdot}80} \text{ gm. potassium}$$

$$= 39{\cdot}20 \text{ gm. potassium.}$$

i.e. Equivalent of potassium = 39·20.

METHOD 4. — You will probably have dipped the blade of your penknife into a solution of copper sulphate. If so, you noticed that the steel became coated with a layer of copper. Actually, there was an exchange of metals, for some of the iron dissolved, forming iron sulphate, and in doing so it deposited copper from solution on to the knife blade. The copper is said to be displaced by the iron. Zinc and magnesium will also displace copper from a solution of copper sulphate, and zinc displaces lead from a solution of lead acetate.

From what you know of equivalents you will realize that the equivalent weight of copper will be displaced by the equivalent weight of zinc, iron, or magnesium, and so, if the equivalent of one metal is known, that of the other can be calculated.

Equivalent of zinc by displacement of copper.— Weigh out accurately about 1 gm. of powdered zinc and place it in a solution of copper sulphate in a beaker. A reddish deposit of copper is seen to form. When the zinc has dissolved, filter off the copper, wash the residue with warm water, dry in a steam oven, and weigh. The calculation is quite simple, as in the following example:

0·98 *gm. of zinc were found to displace* 0·95 *gm. of copper from a solution of copper sulphate. If the equivalent of copper is* 31·8, *calculate the equivalent of zinc.*

0·95 gm. copper is displaced by 0·98 gm. zinc.

$$\therefore\ 31{\cdot}8 \text{ gm. copper are displaced by } \frac{0{\cdot}98 \times 31{\cdot}8}{0{\cdot}95} \text{ gm. zinc}$$
$$= 32{\cdot}8 \text{ gm. zinc.}$$

i.e. Equivalent of zinc = 32·8.

QUESTIONS

1. What is meant by the term *equivalent of an element*? Describe an experiment by which you could determine the equivalent of zinc.

2. What is meant by the term *gramme-equivalent of an element*? Describe in outline two methods by which the equivalent of magnesium may be determined.

3. If you were given some copper sulphate and some zinc, how would you measure the equivalent of copper, if you knew that the equivalent of zinc is 32·5?

4. It was found that 0·67 gm. of a metal when dissolved in dilute hydrochloric acid displaced 0·056 gm. of hydrogen. Calculate the equivalent of the metal.

5. 0·97 gm. of a metal when dissolved in a dilute acid were found to displace 0·035 gm. of hydrogen. Calculate the equivalent of the metal.

6. 0·42 gm. of a metal when dissolved in a dilute acid liberated 78·5 c.c. of hydrogen. The temperature of the laboratory was 14° C. and the air pressure was 77·8 cm. of mercury. Calculate the equivalent of the metal. (1 litre of hydrogen at S.T.P. weighs 0·09 gm.)

7. 0·61 gm. of a metal when dissolved in a dilute acid liberated 112 c.c. of hydrogen. The temperature of the laboratory was 12·5° C. and the air pressure was 76·9 cm. of mercury. Calculate the equivalent of the metal. (1 litre of hydrogen at S.T.P. weighs 0·09 gm.)

8. It was found that 1·09 gm. of a metal gave on oxidation 1·36 gm. of oxide. Calculate the equivalent of the metal.

9. It was found that 1·05 gm. of a metal gave on oxidation 1·19 gm. of oxide. Calculate the equivalent of the metal.

10. 1·05 gm. of a metallic oxide gave on reduction 0·84 gm. of the metal. Calculate the equivalent of the metal.

11. 1·32 gm. of a metallic oxide gave on reduction 1·22 gm. of the metal. Calculate the equivalent of the metal.

12. 0·691 gm. of iron when placed in a solution of copper sulphate was found to displace 0·792 gm. of copper. If the equivalent of copper is taken to be 31·8, calculate the equivalent of iron.

13. 1·083 gm. of zinc when placed in a solution of copper

sulphate was found to displace 1·06 gm. of copper. If the equivalent of copper is taken to be 31·8, calculate the equivalent of zinc.

14. 9·09 gm. of a metallic chloride was dissolved in water and silver nitrate solution was added. The resulting precipitate of silver chloride was found to weigh 17·47 gm. Assuming that every 143·5 gm. of silver chloride contains 35·5 gm. of chlorine, and that the equivalent of chlorine is 35·5, calculate the equivalent of the metal.

15. 3·51 gm. of a metallic chloride was dissolved in water and silver nitrate solution was added. The resulting precipitate of silver chloride was found to weigh 8·61 gm. Assuming that every 143·5 gm. of silver chloride contains 35·5 gm. of chlorine, and that the equivalent of chlorine is 35·5, calculate the equivalent of the metal.

CHAPTER VII

ATOMIC WEIGHT: MOLECULAR WEIGHT: FORMULÆ: VALENCY: EQUATIONS

ATOMIC WEIGHT

All atoms of the same element have the same weight, different from the weights of atoms of other elements. These weights have been ascertained, but the methods for doing so are very difficult and cannot be explained at this stage. Moreover, the actual weights of atoms are so very small as to be of little use to us. What are of great importance to us are the *relative* weights of different atoms. These can be readily determined, and a list of them is given at the end of the book (p. 279).

It is found that the hydrogen atom is the lightest, and so it is convenient to call this 1. The weights of all the other atoms are stated in relation to the weight of a hydrogen atom, and these weights are called the **atomic weights** of the elements. For example, when we say that the atomic weight of oxygen is 16, we mean that every oxygen atom weighs 16 times as much as every hydrogen atom.

The atomic weight of an element is the weight of an atom of that element relative to the weight of a hydrogen atom.

MOLECULAR WEIGHT

It is found that a molecule of sodium chloride (common salt) contains 1 atom of sodium combined with 1 atom of chlorine. That being so, it is clear that the weight of the sodium chloride molecule is equal to the sum of the atomic weights of sodium and chlorine. These are 23

and 35·5 respectively. That is, the weight of a molecule of sodium chloride is $23 + 35{\cdot}5 = 58{\cdot}5$, relative to the weight of a hydrogen atom. This number is called the **molecular weight** of sodium chloride.

The molecular weight of a compound is the weight of a molecule of that compound relative to the weight of an atom of hydrogen.

FORMULÆ

You have, of course, seen formulæ and equations in chemistry textbooks and have possibly felt something like alarm at the thought of having to learn them. What an unnecessary complication, you may have thought, to introduce into an otherwise interesting subject a lot of lettering and equations that seem to convey nothing but have every appearance of being very complicated and difficult to learn.

That is a wrong idea entirely. Formulæ and equations were not introduced to make things harder, but to make things easier and more completely understood. You must also get rid of the entirely wrong notion, if you had it, that formulæ constitute a kind of chemical shorthand. If we wanted to express, for example, " sugar " in a shorthand way we should certainly not write $C_{12}H_{22}O_{11}$ — it is far easier to write " sugar " in long-hand; we couldn't possibly compete with genuine shorthand systems! No, formulæ were introduced to enable us to see things more clearly and to express a great many chemical truths in a little group of letters and figures. It may make chemistry a little harder at first — just as learning multiplication tables made your arithmetic harder at first — but it will make it very much easier and more interesting later on.

We represent *atoms* of elements by letters, either a single capital letter or two letters, the first a capital. For example, a hydrogen atom is represented by the letter H, an oxygen atom by the letter O, and a carbon

atom by C. Sometimes, of course, we find other elements whose names begin with letters which we are already using as symbols. In the above cases this occurs. A helium atom cannot be represented by H, as that is already used for hydrogen, and so it is written He. There are other elements beginning with H, but you will not be troubled with them for some time. Calcium, cobalt, chlorine, chromium, and copper, like carbon, begin with a C, and their atoms are represented by Ca, Co, Cl, Cr, and Cu respectively. (Cu, coming from the Latin *cuprum*, is used; Co cannot be used for copper, being already attached to cobalt.) You will find the formulæ of elements given with the list of atomic weights at the end of the book (p. 279).

Although H stands for an atom of hydrogen, you will generally see hydrogen in an equation represented as H_2. This stands for two hydrogen atoms combined to form a molecule of hydrogen. This gas, when it exists alone, goes about in pairs of atoms, that is, the molecule of hydrogen contains two atoms. A number of other elements behave in the same way, the most common of which is oxygen. O stands for an atom of oxygen; O_2 stands for a molecule of oxygen, which contains two atoms.

If we wish to represent a single atom of hydrogen we write H, and 2H if we mean two single atoms of hydrogen.

You know from the atomic theory that small numbers of atoms of two or more elements combine to form compounds. One atom of sodium combines with one of chlorine to form a molecule of sodium chloride. This is represented by NaCl. Remember that NaCl stands for one molecule of sodium chloride; it is not shorthand for " salt ".

Two atoms of hydrogen combine with one of oxygen to form a molecule of water, and this is represented by H_2O. Notice that the 2 after the H means two atoms of hydrogen, not two of oxygen.

In the example quoted earlier in this chapter,

$C_{12}H_{22}O_{11}$ stands for a molecule of sugar, and the formula tells us that the sugar molecule is made up of a combination of 12 atoms of carbon, 22 of hydrogen, and 11 of oxygen.

Sometimes you see a number *before* a formula. This means that particular number of whole molecules of that substance: $2H_2O$ means two molecules of water, each consisting of a combination of two atoms of hydrogen with one of oxygen: 3NaCl means three molecules of sodium chloride, each consisting of a combination of one atom of sodium with one of chlorine.

You will often see brackets used, for example, $Cu(NO_3)_2$. The number after the bracket means that the part of the molecule inside the bracket is multiplied by that number. The substance, copper nitrate, could therefore have its molecule expressed: CuN_2O_6. We write it $Cu(NO_3)_2$ because it is a nitrate, derived from nitric acid, which has the formula HNO_3; nitrates in general have the formula $X_m(NO_3)_n$, where m and n are small whole numbers. The NO_3 part of the formula is kept as such so that the substance is easily recognizable as a nitrate; NO_3 is called the nitrate *radical.*

VALENCY

Whenever atoms of elements combine they do so in simple small numbers. Let us consider some examples of this.

One atom of hydrogen and one atom of chlorine combine to form a molecule of hydrogen chloride, HCl.

Hydrogen combines with oxygen, however, in the ratio of *two* atoms of hydrogen to one of oxygen, to form a molecule of water, H_2O.

Hydrogen combines with nitrogen in the ratio of *three* atoms of hydrogen to one of nitrogen, to form a molecule of ammonia, NH_3.

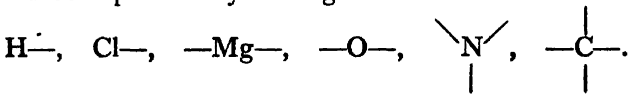
Hydrogen combines with carbon in the ratio of *four* atoms of hydrogen to one of carbon, to form a molecule of methane, CH_4.

The *valency* of chlorine, oxygen, nitrogen, and carbon is said to be 1, 2, 3, and 4, respectively. Or, chlorine, oxygen, nitrogen, and carbon are said to be univalent, bivalent, tervalent, and quadrivalent, respectively.

Similarly, one atom of sodium displaces one atom of hydrogen, one atom of magnesium displaces two atoms of hydrogen. The valencies of sodium and magnesium are 1 and 2, respectively.

The valency of an element is the number of hydrogen atoms that will combine with, or be displaced by, one atom of the element.

It is seen, then, that the valency of an element may be regarded as, so to speak, its atomic equivalent, or as its combining power. We may regard it as if the hydrogen and chlorine atoms have one unit of combining power each, magnesium and oxygen have two each, nitrogen has three, and carbon has four. This could be expressed by writing the formulæ:



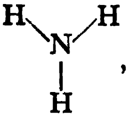
Compounds may be represented thus:

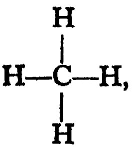
H—Cl, hydrogen chloride, HCl.

H—O—H, water, H_2O.

Cl—Mg—Cl, magnesium chloride, $MgCl_2$.

Mg=O, magnesium oxide, MgO.


, ammonia, NH_3.


, methane, CH_4.

O=C=O, carbon dioxide, CO_2.

Formulæ written in this way, showing the valency bonds, are not often met with in elementary inorganic chemistry. In organic chemistry, however, where the molecular structure is of great importance, we use them considerably. They are also used to some extent in more advanced inorganic chemistry.

Relation between atomic weight, equivalent, and valency

We have said that the valency of an element is, so to speak, its "atomic equivalent". Let us consider the valencies and equivalents in a few cases.

(*a*) Chlorine has an atomic weight of 35·5, and a valency of 1, i.e. 1 atom of hydrogen, weighing 1 unit, combines with 1 atom of chlorine, weighing 35·5 units.

∴ the combining weights of hydrogen and chlorine are as 1 : 35·5,

∴ the equivalent of chlorine is 35·5.

The equivalent of a univalent element is the same as its atomic weight.

(*b*) Oxygen has an atomic weight of 16 and a valency of 2, i.e. 2 atoms of hydrogen, weighing together 2 units, combine with 1 atom of oxygen, weighing 16 units.

∴ the combining weights of hydrogen and oxygen are as 2 : 16 = 1 : 8,

∴ the equivalent of oxygen is 8.

The equivalent of a bivalent element is half its atomic weight.

Similar arguments in cases of tervalent and quadrivalent elements will show that the equivalents are one-third and one-quarter of the atomic weights respectively.

We see, then, that the equivalent is the atomic weight divided by the valency, or

ATOMIC WEIGHT = EQUIVALENT × VALENCY.

EQUATIONS

Whenever a chemical change takes place it is a change between atoms, and so can readily be represented by formulæ.

You have seen magnesium burning in air — it does so with a brilliant white flame and produces magnesium oxide, a white powder. What happens, expressed chemically, is that magnesium combines with oxygen, which is present in the air, forming the compound magnesium oxide. We may represent this change as follows:

$$2Mg + O_2 \rightarrow 2MgO.$$

This means that two molecules of magnesium (each consisting of one atom) combine with one molecule of oxygen (consisting of two atoms) and produce two molecules of magnesium oxide (each consisting of one atom of magnesium combined with one atom of oxygen).

From the law of conservation of matter, and from your knowledge of atoms, you must realize that there can be no gain or loss of matter; the atoms are merely re-arranged. So it is clear that in the above case the weight of two atoms of magnesium plus the weight of a molecule of oxygen is equal to the weight of two molecules of magnesium oxide. The above statement, then, is really an *equation*, and so may be written:

$$2Mg + O_2 = 2MgO.$$

If the atomic weights of the elements concerned are known, it is possible to calculate many things from formulæ and equations. Examples of some of these are given below.

CALCULATIONS INVOLVING FORMULÆ AND EQUATIONS

1. Percentage composition of a compound from the formula

(*a*) Let us take for our first example sodium chloride. Its formula is NaCl. This represents, as we have seen, a molecule of sodium chloride, and shows that the molecule contains one atom of sodium and one of chlorine.

The atomic weights of sodium and chlorine are 23 and 35·5 respectively. Therefore the molecular weight of sodium chloride is 58·5.

Since a molecule of sodium chloride contains one atom of sodium, 58·5 parts by weight of sodium chloride contain 23 parts by weight of sodium.

58·5 gm. of sodium chloride contain 23 gm. of sodium.

$\therefore$ 1 " " " " $\dfrac{23}{58{\cdot}5}$ "

$\therefore$ 100 " " " " $\dfrac{23 \times 100}{58{\cdot}5}$ "

$= 39{\cdot}3$ gm. of sodium.

Similarly,

58·5 gm. of sodium chloride contain 35·5 gm. of chlorine.

$\therefore$ 1 " " " " $\dfrac{35{\cdot}5}{58{\cdot}5}$ "

$\therefore$ 100 " " " $\dfrac{35{\cdot}5 \times 100}{58{\cdot}5}$ "

$= 60{\cdot}7$ gm. of chlorine.

That is, the percentage composition of sodium chloride is:

sodium 39·3 per cent, chlorine 60·7 per cent.

Another example with a somewhat more complicated molecule should make this type of calculation quite clear.

(*b*) *Calculate the percentage composition of potassium sulphate, the formula being* K_2SO_4.

A molecule of potassium sulphate contains 2 atoms of

potassium, 1 of sulphur, and 4 of oxygen. The atomic weights of these three elements are 39, 32, and 16 respectively.

2 atoms of potassium weigh	$2 \times 39 =$	78	units.
1 ,, sulphur ,,	$1 \times 32 =$	32	,,
4 ,, oxygen ,,	$4 \times 16 =$	64	,,
1 molecule of potassium sulphate weighs		174	,,

i.e. molecular weight of potassium sulphate is 174.

174 gm. of potassium sulphate contain 78 gm. of potassium.

$\therefore$ 1 ,, ,, ,, ,, $\frac{78}{174}$,,

$\therefore$ 100 ,, ,, ,, ,, $\frac{78 \times 100}{174}$,,

$= 44{\cdot}8$ gm. of potassium.

174 gm. of potassium sulphate contain 32 gm. of sulphur.

$\therefore$ 1 ,, ,, ,, ,, $\frac{32}{174}$,,

$\therefore$ 100 ,, ,, ,, ,, $\frac{32 \times 100}{174}$,,

$= 18{\cdot}4$ gm. of sulphur.

174 gm. of potassium sulphate contain 64 gm. of oxygen.

$\therefore$ 1 ,, ,, ,, ,, $\frac{64}{174}$,,

$\therefore$ 100 ,, ,, ,, ,, $\frac{64 \times 100}{174}$,,

$= 36{\cdot}8$ gm. of oxygen.

That is, the percentage composition of potassium sulphate is:

Potassium 44·8 per cent, sulphur 18·4 per cent,
oxygen 36·8 per cent.

2. Empirical formula of a compound from the percentage composition

This is the reverse of the previous problem. We will start with a simple example and then have a more complicated (though no more difficult) one.

(*a*) *The composition of potassium chloride is found to be: Potassium* 52·5 *per cent, chlorine* 47·5 *per cent. Calculate the empirical formula.* (K = 39, Cl = 35·5.)

52·5 gm. of potassium combine with 47·5 gm. of chlorine. Dividing each quantity by the respective atomic weight, we get:

$\frac{52 \cdot 5}{39}$ *atoms* of potassium combine with $\frac{47 \cdot 5}{35 \cdot 5}$ *atoms* of chlorine.

i.e. 1·34 ,, ,, ,, ,, 1·34 ,, ,,

But as atoms are indivisible, we cannot possibly have 1·34 atoms.

∴ 1 atom of potassium combines with 1 atom of chlorine to form 1 molecule of potassium chloride,

i.e. formula of potassium chloride is KCl.

Note. — This formula, KCl, is only the simplest formula. Our result would also satisfy the formula K_2Cl_2, or K_3Cl_3, etc. We have here no reason for knowing which is correct, so we take the simplest formula, or *empirical formula*, as it is called. This is KCl.

(*b*) *The composition of potassium chlorate is found to be:* 31·8 *per cent potassium,* 29·0 *per cent chlorine, and* 39·2 *per cent oxygen. Calculate the empirical formula.* (K = 39, Cl = 35·5, O = 16.)

The combining weights of the three elements are:

	Potassium	*Chlorine*	*Oxygen*
	31·8	29·0	39·2

(Dividing each by the respective atomic weights:)

	$\frac{31 \cdot 8}{39}$ *atoms*	$\frac{29 \cdot 0}{35 \cdot 5}$ *atoms*	$\frac{39 \cdot 2}{16}$ *atoms*
or	·815 atoms	·817 atoms	2·45 atoms.

(As we cannot have less than one atom, divide by the smallest to get 1):

1 atom	1 atom	3 atoms

The simplest conception of a molecule of potassium chlorate is one that contains 1 atom of potassium, 1 of chlorine, and 3 of oxygen.

∴ empirical formula of potassium chlorate is $KClO_3$.

3. Reacting quantities from equations

If we know the equation for a chemical reaction it is quite a simple matter to work out the reacting quantities. Consider the two following examples.

(*a*) *What weight of copper can be obtained by reducing* 5 *gm. of copper oxide?* (Cu = 64, O = 16.)

The equation for the reaction is: $CuO + H_2 = H_2O + Cu$.

We now find the molecular weights for the substances concerned, thus:

$$\begin{array}{ccccccc} \text{Cu} & \text{O} & + \ \text{H}_2 & = & \text{H}_2 & \text{O} & + \ \text{Cu} \\ \multicolumn{2}{c}{\underbrace{64 + 16}_{80}} & 2 & & \multicolumn{2}{c}{\underbrace{2 + 16}_{18}} & 64 \\ & & 2 & & & & 64 \end{array}$$

That is, as one of the things that the equation tells us is that one molecule of copper oxide gives one molecule (= 1 atom) of copper, we can say that 80 parts by weight of copper oxide give 64 parts by weight of copper.

(Note that we disregard the weights of hydrogen and water, as they are not concerned with the particular question.)

80 gm. of copper oxide give 64 gm. of copper.

$\therefore$ 1 ,, ,, ,, ,, $\frac{64}{80}$,,

$\therefore$ 5 ,, ,, ,, ,, $\frac{64 \times 5}{80}$,,

= 4 gm. of copper.

(*b*) *What weight of hæmatite (one of the ores of iron) is necessary to produce* 50 *tons of iron?*

The formula for hæmatite is Fe_2O_3, and the equation for the reduction of this oxide to the metal is: $Fe_2O_3 + 3CO = 2Fe + 3CO_2$. (Fe = 56, O = 16.)

$$\begin{array}{ccccc} \text{Fe}_2 \quad \text{O}_3 & + \ 3\text{CO} & = & 2\text{Fe} & + \ 3\text{CO}_2 \\ \underbrace{2 \times 56 + 3 \times 16}_{160} & & & \underbrace{2 \times 56}_{112} & \end{array}$$

i.e. 112 tons of iron are produced from 160 tons of hæmatite.

$\therefore$ 1 ,, ,, is ,, ,, $\frac{160}{112}$,, ,,

$\therefore$ 50 ,, ,, are ,, ,, $\frac{160 \times 50}{112}$,, ,,

= 71·4 tons of hæmatite.

QUESTIONS

1. What is meant by: *atomic weight, molecular weight, symbol, formula?*

2. Explain what is meant by the following equations:
(*a*) $C + O_2 = CO_2$.
(*b*) $2Hg + O_2 = 2HgO$.
(*c*) $CaCO_3 = CaO + CO_2$.
(*d*) $KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$.
(*e*) $3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O$.

3. Calculate the percentage composition of:
(*a*) Carbon dioxide, CO_2;
(*b*) Potassium chloride, KCl;
(*c*) Potassium nitrate, KNO_3;
(*d*) Ammonium sulphate, $(NH_4)_2SO_4$;
(*e*) Sulphuric acid, H_2SO_4.

4. Calculate the percentage water of crystallization in:
(*a*) Copper sulphate crystals, $CuSO_4{\cdot}5H_2O$;
(*b*) Zinc sulphate crystals, $ZnSO_4{\cdot}7H_2O$;
(*c*) Washing soda crystals, $Na_2CO_3{\cdot}10H_2O$.

5. Calculate the empirical formulæ for substances having the following percentage compositions:
(*a*) Carbon 42·9, oxygen 57·1;
(*b*) Aluminium 52·9, oxygen 47·1;
(*c*) Calcium 40, carbon 12, oxygen 48;
(*d*) Calcium 54·1, oxygen 43·2, hydrogen 2·7;
(*e*) Potassium 26·5, chromium 35·4, oxygen 38·1.

6. What weight of sodium chloride can be obtained from 5 gm. of sodium hydroxide?

$$NaOH + HCl = NaCl + H_2O.$$

7. How many tons of iron can be obtained from 50 tons of hæmatite?

$$Fe_2O_3 + 3CO = 3CO_2 + 2Fe.$$

8. How many tons of limestone are necessary to produce 10 tons of quicklime?

$$CaCO_3 = CaO + CO_2.$$

CHAPTER VIII

AVOGADRO'S HYPOTHESIS AND MOLECULAR WEIGHTS

In 1804 Joseph Louis Gay-Lussac, a French chemist, made a series of experiments to investigate the proportions in which gases combine. He obtained a remarkable result, which may be summed up as follows:

Gay-Lussac's Law of Gaseous Volumes

The volumes in which two gases combine are in a simple ratio to each other, and to that of the product, if this is a gas.

The meaning of this will become quite clear if you will study the following examples:

1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.

2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam.

1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia.

This discovery is very important: out of the infinite number of different proportions in which gases could combine, they *all* do so in simple small ratios by volume, such as 1 to 1, 1 to 2, 2 to 3, and so on. It is clear that there must be some reason for this, and it may help us to see what happens to the particles of the gases when they react. This being so, it might be profitable to examine these facts in the light of the atomic theory, published by Dalton a little before Gay-Lussac's discovery. This was, in fact, done, and it caused quite a lot of trouble, for it was found that Gay-Lussac's law and Dalton's theory could not be reconciled.

To illustrate this, let us consider the case of the combination of chlorine and hydrogen.

1 volume of hydrogen combines with 1 volume of chlorine. (Gay-Lussac)
1 atom of hydrogen combines with 1 atom of chlorine. (Dalton)
∴ 1 volume of chlorine and 1 volume of hydrogen contain equal numbers of atoms.

A number of chemists came to more or less this conclusion, which might be expressed generally: "Equal volumes of different gases contain equal numbers of atoms."

(The word "atoms" was then used to include what we now call "molecules" as well as what we now call "atoms".)

Let us continue with our consideration of the combination of hydrogen and chlorine, including the gaseous product, hydrogen chloride.

1 volume of hydrogen combines with 1 volume of chlorine, giving 2 volumes of hydrogen chloride.

By our conclusion arrived at above:

1 *atom* of hydrogen combines with 1 *atom* of chlorine giving 2 "*atoms*" of hydrogen chloride.

But as each "atom" of hydrogen chloride must contain both hydrogen and chlorine, and as 2 atoms of hydrogen chloride were formed from only 1 of hydrogen and 1 of chlorine, then each hydrogen chloride "atom" can contain only half an atom of hydrogen and half an atom of chlorine.

This clearly strikes at the very foundation of Dalton's atomic theory, which states that atoms are indivisible.

It was Amedeo Avogadro, an Italian, who a few years later (1811) overcame this difficulty of reconciling Gay-Lussac's law with Dalton's atomic theory. His hypothesis to explain Gay-Lussac's results was not accepted for forty years — until after his death, in fact.

Avogadro's hypothesis. — *Equal volumes of all*

gases, at the same temperature and pressure, contain equal numbers of molecules.

Vapour Density

Avogadro, seeing the difficulty of Gay-Lussac's results suggesting half-atoms, suggested instead that both hydrogen and chlorine gases existed, not as single atoms, but in pairs of atoms. The smallest part of an element that can exist alone, he said, is not necessarily an atom; in each of the above two cases it is two atoms. Avogadro called these smallest particles " molecules ".

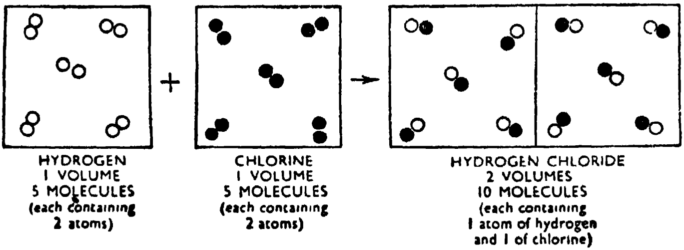


Fig. 10

We will now see how Avogadro's hypothesis makes Gay-Lussac's law fit in with Dalton's atomic theory.

1 volume of hydrogen combines with 1 volume of chlorine to give 2 volumes of hydrogen chloride.

1 molecule (containing 2 atoms) of hydrogen combines with 1 molecule (containing 2 atoms) of chlorine to give 2 molecules (each containing 1 atom of hydrogen and 1 of chlorine) of hydrogen chloride.

If we could obtain such a small volume of gas that it would contain only 5 molecules, we could represent the combination of 5 molecules of chlorine and 5 of hydrogen as in fig. 10.

The question may now arise: how is it that equal volumes of different gases can contain equal numbers of

molecules, if the molecules are of different sizes, as, for example, hydrogen and carbon dioxide?

The answer is that while it is true that the molecules of carbon dioxide are considerably bigger and heavier than those of hydrogen, they are more closely packed in the former, although there is considerable space between the molecules in each gas. The actual molecules of a gas are flying about at high speeds, and colliding with one another and with the walls of the containing vessel, if

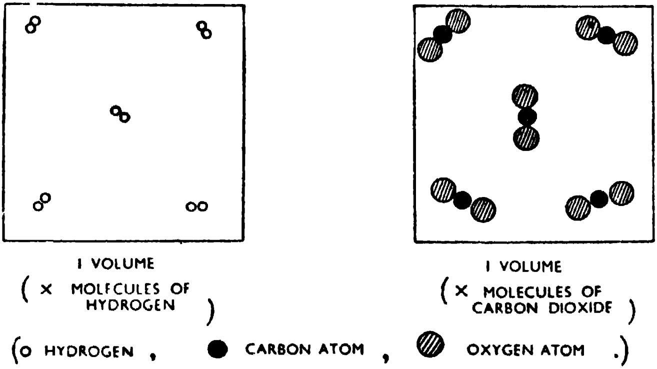


Fig. 11

any. Their total volume is only a very small portion of the space occupied by the gas (fig. 11).

One reason why Avogadro's hypothesis is of great importance is that we can deduce from it the following relation between molecular weight and vapour density:

The molecular weight of a substance is twice its vapour density.

We do not measure densities of gases as absolute densities, i.e. in grammes per cubic centimetre, because the value would be a very small number and not very useful to us. It is far more useful to express it as the density relative to hydrogen. For example, the density of carbon dioxide is said to be 22, and by this we mean that its density is 22 times that of hydrogen.

By the **vapour density** of a substance not a gas, we mean the density, relative to hydrogen, of that substance if it is converted into the gaseous state. The density of water (liquid) is, as you know, 1 gm. per cubic centimetre. The vapour density of water is 9; that is, water in the gaseous state (steam) is 9 times as dense as hydrogen, under the same conditions of temperature and pressure.

$$\text{Vapour density} = \frac{\text{weight of a certain volume of gas}}{\text{weight of same volume of hydrogen}}$$

$$= \frac{\text{weight of } x \text{ molecules of substance}}{\text{weight of } x \text{ molecules of hydrogen}}$$

$$= \frac{\text{weight of 1 molecule of substance}}{\text{weight of 1 molecule of hydrogen}}.$$

But, as we have previously argued, each molecule of hydrogen contains 2 atoms.

$$\text{Vapour density} = \frac{\text{weight of 1 molecule of substance}}{\text{weight of 2 atoms of hydrogen}}$$

$$= \frac{1}{2}\,\frac{\text{weight of 1 molecule of substance}}{\text{weight of 1 atom of hydrogen}}$$

$$= \tfrac{1}{2} \text{ molecular weight of substance.}$$

i.e. *the molecular weight of a substance is twice its vapour density.*

Hence if we can measure the vapour density of a substance, we can calculate its molecular weight.

Another important conclusion from Avogadro's hypothesis is that the molecular weight in grammes of a substance in the gaseous state occupies 22·4 litres at S.T.P.

It is found by experiment that 1 gm. of hydrogen occupies 11·2 litres at S.T.P.

But the gramme-molecular weight of hydrogen is 2 gm.

$\therefore$ 2 gm. of hydrogen occupy 22·4 litres.

Now consider a gas of molecular weight x. Its density relative to hydrogen is, as we have seen, $\frac{1}{2}x$.

∴ $\frac{1}{2}x$ gm. of gas has the same volume as 1 gm. of hydrogen.

∴ x gm. of gas has the same volume as 2 gm. of hydrogen, which is 22·4 litres.

i.e. *The molecular weight in grammes of any gas occupies 22·4 litres at S.T.P.*

Determination of vapour density

The vapour density of a gas is found by weighing a glass globe which has had all the air expelled from it by means of a vacuum pump, and then weighing it full of the gas, and subsequently full of hydrogen.

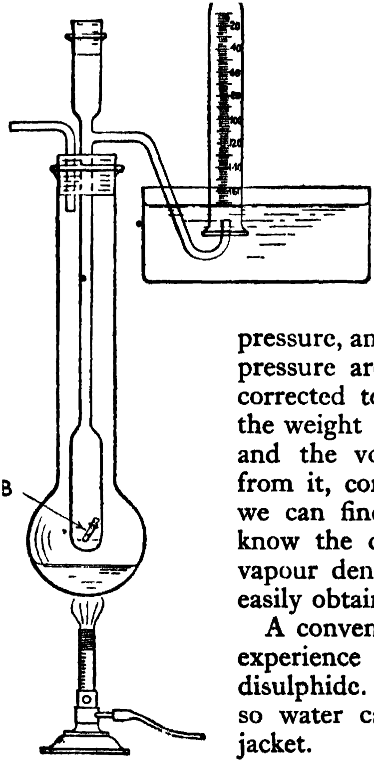
Subtracting the weight of the glass globe from each of the other two weights, we get weights of equal volumes of the gas and hydrogen. The vapour density of the gas is then $\frac{\text{weight of gas}}{\text{weight of hydrogen}}$.

The vapour density of a volatile liquid may be found by a very ingenious method devised by the German chemist Victor Meyer.

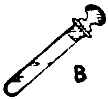
The apparatus is shown in fig. 12 (p. 68). The liquid whose vapour density is to be found is weighed accurately in a small bottle B. Meanwhile the liquid in the outer jacket, of boiling-point higher than that of the liquid whose vapour density we are finding, is boiled. The air in the inner tube expands and bubbles out into the trough, the gas cylinder being removed. When no more air bubbles into the trough, it means that the air in the inner tube has reached the boiling-point of the liquid in the outer jacket.

The gas cylinder is now placed in position, the cork at the top of the inner tube removed, the bottle B dropped in, and the cork immediately replaced. A little asbestos fibre in the bottom of the outer vessel will prevent breakage when the bottle is dropped in.

The liquid in the little tube, being surrounded by an atmosphere at a higher temperature than its own boiling-point, now begins to boil, and it forces out its little glass stopper and begins to evaporate quickly. The volume



of vapour formed from it expels an equal volume of air from the inner tube into the gas cylinder. This volume of air is measured at atmospheric



pressure, and the air temperature and pressure are noted. The volume is corrected to S.T.P. Thus we have the weight of a sample of the liquid, and the volume of vapour formed from it, corrected to S.T.P., and so we can find its density, and if we know the density of hydrogen, the vapour density of the liquid can be easily obtained.

A convenient liquid to use to gain experience in this method is carbon disulphide. It boils at 46·25° C., and so water can be used in the outer jacket.

Fig. 12 — Determination of Vapour Density of a Volatile Liquid.

EXAMPLE. — ·182 gm. of carbon disulphide expelled 59·9 c c. of air from the inner tube. The air temperature was 12° C. and the air pressure was 75 6 cm.

First correct the gas to S.T.P.:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2},$$

$$\frac{75{\cdot}6 \times 55{\cdot}9}{285} = \frac{76V_2}{273},$$

$$V_2 = \frac{75{\cdot}6 \times 55{\cdot}9 \times 273}{76 \times 285} = 53{\cdot}28 \text{ c.c.}$$

i.e. 53·28 c.c. carbon disulphide at S.T.P. weigh ·182 gm.

$\therefore$ 1000 c.c. ,, ,, ,, ,, $\frac{\cdot 182 \times 1000}{53 \cdot 28}$ gm.

But 1000 c.c. of hydrogen weigh ·09 gm.

$\therefore$ Density of carbon disulphide $(H = 1) = \frac{\cdot 182 \times 1000}{53 \cdot 28 \times \cdot 09} = 38.$

(The molecular weight is, of course, twice this, i.e. 76.)

QUESTIONS

1. State Gay-Lussac's law of gaseous volumes.

2. State Avogadro's hypothesis. What is its importance in chemistry?

3. Deduce from Avogadro's hypothesis the relationship between the vapour density of a gas and its molecular weight.

4. Describe Victor Meyer's method for measuring the vapour density of a volatile liquid.

5. In a Victor Meyer experiment, 0·25 gm. of a volatile liquid expelled 54·8 c.c. of air at S.T.P. Calculate the vapour density of the liquid.

6. In a Victor Meyer determination, 0·4 gm. of a volatile liquid displaced 100 c.c. of air. The temperature of the laboratory was 14° C., and the barometer read 756 mm. Calculate the molecular weight of the liquid.

CHAPTER IX

CHEMICAL EQUILIBRIUM AND CATALYSIS

If calcium carbonate is heated strongly the molecule splits up into two parts, carbon dioxide, a gas, being evolved and calcium oxide, a white solid, being left. The calcium carbonate is said to *dissociate* into carbon dioxide and calcium oxide:

$$CaCO_3 = CaO + CO_2.$$

This chemical change is generally made to take place under conditions when the carbon dioxide is allowed to escape, and it is found that then the whole of the calcium carbonate is decomposed.

If, however, carbon dioxide is passed over calcium oxide the reverse action takes place and calcium carbonate is formed:

$$CaO + CO_2 = CaCO_3.$$

Let us examine the difference between these two actions and see why one should proceed in one direction and the other in the opposite direction.

There is a tendency for calcium carbonate to split up into calcium oxide and carbon dioxide, and there is also a tendency for calcium oxide and carbon dioxide to combine to form calcium carbonate. In the first case the gas carbon dioxide is allowed to escape and so there is not very much of it round the calcium oxide to combine with it and form the carbonate. More calcium carbonate then decomposes, forming more calcium oxide, and more

carbon dioxide passes away from the sphere of the reaction. This continues until all the calcium carbonate is decomposed.

In the second case, where the gas is passed over the solid, the calcium oxide is surrounded by an atmosphere of carbon dioxide and so there is every encouragement for the molecules to combine, forming calcium carbonate.

Now suppose we heat calcium carbonate in a closed vessel, so that none of the carbon dioxide can escape. We should expect both reactions to occur, and this is indeed the case. Calcium carbonate splits up into calcium oxide and carbon dioxide, and these in turn combine to form calcium carbonate again. Very soon there is found to be a definite amount of each constituent present and these amounts remain constant if the temperature is kept the same. This can be proved by attaching a pressure gauge to the vessel. The pressure is found to remain constant, and as this pressure can only be due to the carbon dioxide (the only gas present) it means that the amount of carbon dioxide there remains constant.

This does not mean that a deadlock is reached and the two opposing chemical reactions decide to "call it a day" and refuse to go on reacting. Change is constantly occurring, but the reactions adjust themselves so that the speed of the forward change is equal to that of the backward change. The substances are said to be in a state of **chemical equilibrium**, and the changes are generally represented by an equation in the form:

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

Such a change is called a **reversible reaction.**

Let us return again to a consideration of the reaction in a closed vessel. We start with calcium carbonate only. Therefore on first heating the only possible change is decomposition of the carbonate, i.e. the forward reaction. However, when the first few molecules of calcium oxide and carbon dioxide have been formed they start combining to form calcium carbonate, but there are not

many of them. Hence they have not a great opportunity of meeting and reacting, and so the speed of the reverse change is slow. But as more and more of these molecules are formed the likelihood of their meeting is much increased, and the speed with which the reverse action takes place gradually increases until it is equal to the speed of the forward reaction.

So that when a state of equilibrium has been reached the reaction must not be considered to have stopped; the two reactions in opposite directions are proceeding all the time and with equal speeds.

If one of the products of a reversible reaction is removed, then equilibrium is upset and the change proceeds only in one direction. This can be done, as we have seen, if one of the products is a gas, by allowing it to escape. It also occurs in a reaction between two liquids if one of the products is an insoluble solid. Once a substance is precipitated it is out of the sphere of the reaction and does not take part in any reverse change.

For example, when sodium chloride solution and dilute nitric acid are mixed, the reaction is reversible and is represented by

$$NaCl + HNO_3 \rightleftharpoons NaNO_3 + HCl.$$

All the substances are soluble; equilibrium is attained and an analysis of the liquid shows that all four substances are present.

If, however, sodium chloride and silver nitrate solutions are mixed, the reaction proceeds in the forward direction only:

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl.$$

The reason for this reaction not being reversible is that silver chloride is insoluble in water, so that each molecule of it, as soon as it is formed, is precipitated as a solid and cannot take part in the reverse reaction.

This principle is used to a great extent in qualitative and quantitative analysis.

Another good example of a reversible reaction is that between steam and iron.

When steam is passed over red-hot iron, hydrogen is evolved and black oxide of iron is formed:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2.$$

In this reaction the current of steam sweeps away the hydrogen, so that hydrogen molecules do not come into contact with iron oxide molecules.

The reverse change, however, may be made to take place by passing hydrogen over heated iron oxide:

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O.$$

Here it is the current of hydrogen that sweeps away the steam formed, and so the latter cannot come into contact with iron to reform the oxide.

If, however, either iron oxide and hydrogen, or iron and steam, are heated in a closed vessel, all four substances will be found to be present, showing that the reversible reaction has attained equilibrium:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

Law of mass action

The fact that the speed of a chemical change depends on the concentration of the reacting substances is summed up in the **law of mass action**, which may be stated as follows:

The rate of a chemical change is proportional to the concentrations of the reacting substances.

It is seen that in a reversible reaction, e.g. $A + B \rightleftharpoons C + D$, as more and more of A and B react, there is less and less of them, and so the speed $A + B \rightarrow C + D$ decreases. Similarly, as more and more of C and D are formed, the speed of $C+D \rightarrow A+B$ increases. This goes on until such concentrations of A and B and C and D are present that the speeds of the two opposing reactions are equal and equilibrium is attained.

Effect of temperature on rate of chemical change

Place some pieces of granulated zinc in a test-tube and add a few cubic centimetres of dilute sulphuric acid. The reaction proceeds very slowly at first. As the concentrations of zinc and sulphuric acid decrease one would expect the speed of the reaction to lessen. The opposite effect is, however, observed: the reaction speeds up more and more, and finally becomes quite violent for a time, when it begins to slow down and finally stop. The increase in speed in the early part of the reaction indicates that another factor affects the speed of chemical change. This is temperature. When zinc and dilute sulphuric acid react, heat energy is given out, and as the temperature of the mixture rises the speed of the change increases. Most substances give out heat when reacting, and so most chemical changes proceed with increasing speed until the concentrations of the reacting substances diminish considerably.

Also, if a reaction is proceeding slowly, it may generally be speeded up by warming over a Bunsen burner.

Effect of pressure on rate of chemical change

Another factor which changes the speed of a chemical change where gases are concerned is the pressure. Increase in pressure causes the reaction between two gases to proceed more quickly. For the effect of pressure is to diminish the volume, and as chemical change is a change concerning the flying molecules, these, being closer together, will meet more often, and so the rate of the change will be increased.

Catalysis

It is found that the rate of a chemical change may be altered considerably by the presence of another substance which itself undergoes no change. Such a substance is called a *catalyst* and the effect is known as **catalysis**.

A catalyst is a substance which alters the speed of a chemical change but is not changed itself.

Generally we are concerned with catalysts which increase the speed of chemical changes, but occasionally it is necessary to slow down a change which would otherwise be too violent. The catalyst in the latter case is generally called a negative catalyst.

To demonstrate catalysis, heat some powdered crystals of potassium chlorate in an ignition tube, gently at first and then more strongly. The crystals are seen to melt before any gas is given off, and on testing with a glowing splint of wood the latter is rekindled, showing that oxygen is evolved. Now let the tube and contents cool until no more oxygen is being given off, and drop in a little manganese dioxide. The immediate result is the violent evolution of oxygen. This shows that the presence of a little manganese dioxide causes the potassium chlorate to be decomposed at a much lower temperature than by heating it alone. It can be proved that all the manganese dioxide added is still present unchanged after the reaction, showing that the oxygen has come from the potassium chlorate alone, none from the manganese dioxide.

Catalysis is of very great importance to the industrial chemist, for it enables a large-scale process to take place at a much lower temperature than otherwise, and so saves a great amount of fuel. It also enables reactions to take place which cannot be made conveniently to occur without the catalyst, or are so slow otherwise as to be valueless commercially.

It must be understood that it is hardly correct to describe manganese dioxide as a catalyst. It is certainly a catalyst in the decomposition of potassium chlorate by heat, but it can by no means increase the speed of *any* reaction.

Platinum in the finely divided state is a useful catalyst in a number of important chemical changes, notably in the contact process for the manufacture of sulphuric

acid. Other finely divided metals are found to catalyse certain reactions, and are used with great success in industry. Catalysis is one of the most important subjects in modern industrial chemistry, which has been and is being revolutionized by research to find good catalysts.

It is found that in some cases the efficiency of a catalyst can be increased by the addition to it of a small quantity of another substance. In the Haber process for the synthesis of ammonia from nitrogen and hydrogen (see p. 137) the activity of the catalyst — finely divided iron — is increased by the addition of a little molybdenum. A substance which in this way promotes the activity of a catalyst is called a *promotor.*

The activity of a catalyst can also be decreased by the addition of small quantities of certain substances. This is often a nuisance; great care has to be taken in the purification of the reacting substances, otherwise the catalyst quickly becomes " poisoned " and the reaction slows down or stops. Strangely enough, many catalytic poisons are also poisons in the usual sense of the word, arsenic being an example.

QUESTIONS

1. Explain what is meant by the terms *reversible reaction* and *chemical equilibrium.*

2. State and explain the law of mass action.

3. Explain how, in a reversible reaction, the chemical change may be made to proceed in one direction only.

4. Explain the effects of change of temperature and change of pressure on the rate of chemical change.

5. What is a catalyst? Give three examples of processes where a catalyst is employed.

6. Write an account of the importance of catalysis in industrial chemistry, giving examples.

CHAPTER X

ELECTROLYSIS

If wires are connected to the poles of a 2-volt electric battery accumulator and the other ends are dipped into water to which a little sulphuric acid has been added, it is found that the passage of a current of electricity through the liquid causes it to decompose into its elements, hydrogen and oxygen. These gases bubble off from the acidulated water, oxygen at the wire attached to the positive pole of the accumulator and hydrogen at the wire attached to the negative pole.

Such a process is called **electrolysis.**

Electrolysis is the chemical decomposition of a substance by the passage of a current of electricity through it.

The two wires, or more generally plates or rods of metal or carbon, which are in the solution are called **electrodes.** The electrode connected to the positive pole of the battery is called the **anode** and that connected to the negative pole is called the **cathode.** The liquid which is decomposed by the passage of a current of electricity through it is called the **electrolyte.** The vessel in which electrolysis takes place, together with the electrodes and electrolyte, is called the **electrolytic cell,** or **voltameter.**

Fig. 13 (p. 78) should make this clear. The direction of the electric current in the wires and through the electrolyte is shown by arrows.

If electrolysis is attempted with pure distilled water instead of acidulated water, it is found that no gases are evolved and no current is indicated by the ammeter. Many other substances refuse to undergo

electrolysis, for example, sugar dissolved in water, alcohol, and ether. Such substances are called **non-electrolytes.**

Aqueous solutions (solutions in water) of acids, alkalis, and salts are found to be electrolytes, and electrolytic decomposition is found to take place according to definite rules.

It is found that whenever hydrogen is evolved, as it is in the case of acids, this gas is always liberated at the cathode. Whenever metals are deposited, as they are

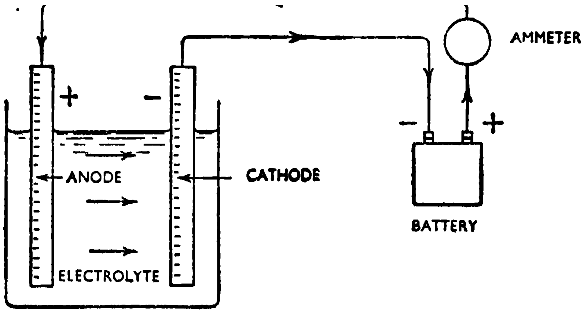


Fig. 13.—The Process of Electrolysis

in the case of alkalis and salts, they are deposited at the cathode. Sometimes, as, for example, with sodium, the metal immediately reacts with the water and a secondary product, hydrogen, is evolved at the cathode.

At the anode we find the non-metallic part of the electrolyte, or its decomposition product, liberated.

For example:

(*a*) Concentrated hydrochloric acid, on electrolysis, gives off chlorine at the anode and hydrogen at the cathode:

$$2HCl = H_2 + Cl_2.$$

(Equal volumes of hydrogen and chlorine, in agreement with Avogadro's hypothesis.)

(*b*) An aqueous solution of sodium chloride on electrolysis gives off chlorine at the anode and sodium at the cathode (see p. 233):

$$2NaCl = 2Na + Cl_2.$$

The chlorine is liberated, but the sodium reacts with water, forming sodium hydroxide and liberating hydrogen:

$$2Na + 2H_2O = 2NaOH + H_2.$$

The result, then, is the liberation of chlorine and hydrogen and the formation of sodium hydroxide. Moreover, the chlorine and sodium hydroxide will react (see p. 159).

(*c*) Copper sulphate solution on electrolysis splits up into copper and " sulphate ":

$$CuSO_4 = Cu + SO_4.$$

The latter is unknown as a separate substance, and immediately reacts with water to form sulphuric acid and liberate oxygen:

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

The net result here, then, is the liberation of oxygen at the anode and the deposition of copper at the cathode.

FARADAY'S LAWS OF ELECTROLYSIS

Michael Faraday in 1834 investigated the phenomenon of electrolysis and discovered that:

(i) *The mass of an element liberated by electrolysis is proportional to the quantity of electricity passed.*

(Quantity of electricity is measured in *coulombs*, and is the product of the current in amperes and the time in seconds.)

(ii) *The masses of different elements liberated by electrolysis by the same quantity of electricity are in the ratio of their chemical equivalents.*

The first law should be quite clear. It says in effect that:

If 1 coulomb	of electricity	liberates	x	gm.	of element,
then 2 coulombs	,,	liberate	$2x$	,,	,,
and 3	,,	,,	$3x$	,,	,,
and Q	,,	,,	Qx	,,	,, .

As Q = current in amperes $\times$ time in seconds,

c amperes for t seconds liberate $c \times t \times x$ gm. of element.

The second law may be illustrated thus:

Suppose voltameters containing various electrolytes are connected in series to a battery, and the substances liberated are, for example, hydrogen, oxygen, chlorine, copper, and zinc.

If the weight of hydrogen liberated in a certain time is x gm., the weights of the other substances liberated in the same time (i.e. by the passage of the same quantity of electricity) are: oxygen $8x$, chlorine $35{\cdot}5x$, copper $31{\cdot}7x$, and zinc $32{\cdot}6x$ gm.

That is, they are liberated in the proportion of their chemical equivalents, which are 8, 35·5, 31·7, and 32·6 respectively.

The quantity of electricity needed to liberate 1 gm. of hydrogen, and therefore also the equivalent of any element, is found by experiment to be 96,000 coulombs. This quantity of electricity is called one *faraday*.

THE IONIC HYPOTHESIS

The theory put forward to explain the facts of electrolysis is known as the Ionic Hypothesis, and it supposes that electrolytes split up into electrically charged parts, called **ions**. This dissociation of a compound into ions occurs whenever an electrolyte is dissolved in water, no matter whether a current of electricity is passing through or not.

The ions have properties entirely different from those of the elements themselves. For example, sodium chloride is an electrolyte, and according to the ionic

hypothesis it is dissociated into sodium ions and chlorine ions when in solution. But *atoms* of sodium react violently with water atoms, and so the ions must have properties quite different from those of the sodium atoms.

The dissociation of sodium chloride on solution is represented thus:

$$NaCl \rightarrow Na^+ + Cl^-$$

The sodium ion is positively charged. When a current of electricity passes through the solution, the sodium

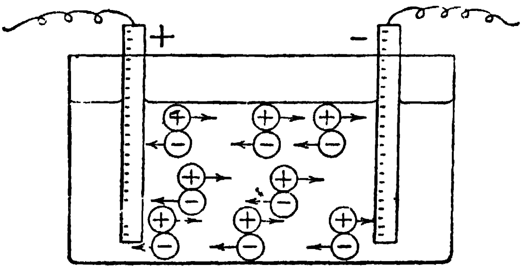


Fig. 14

ions, being positive, are attracted to the negative pole, i.e. the cathode (fig. 14).

Similarly, the chlorine ions, being negatively charged, are attracted to the positive pole, i.e. the anode.

When the positive sodium ions reach the cathode, they give up their charge to it and become ordinary uncharged atoms of sodium. These immediately react with the water molecules and form sodium hydroxide and hydrogen, the latter being observed bubbling from the cathode.

Similarly, the chlorine ions on reaching the anode give up their negative charge to it and become ordinary chlorine atoms, and are evolved as bubbles of gas.

For every sodium ion discharged at the cathode a

chlorine ion is discharged at the anode. Hence it is seen that equal numbers of sodium and chlorine atoms are liberated, and so the two elements will be liberated in the ratio of their equivalents. The equivalent of sodium will displace from water the equivalent of hydrogen, so in the above example it is seen that, arguing from the ionic hypothesis, the hydrogen and the chlorine are evolved in the ratio of their equivalents. This agrees with the experimental results as expressed in Faraday's laws.

Electrolysis of acidulated water

Pure water is not an electrolyte; it is the acid which ionizes in solution, thus:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{--}.$$

(Note that the formula for the hydrogen is $2H^+$ and not H_2. H_2 stands for one molecule of hydrogen, consisting of 2 atoms. 2H stands for 2 single atoms of hydrogen. $2H^+$ stands for two *ions* of hydrogen, positively charged. Note also that the bivalent radical SO_4^{--} carries two units of negative charge, to neutralize the two single charges of the two hydrogen ions.)

When an electric current is passed through acidulated water, the hydrogen ions travel to the cathode, their positive charges are neutralized, and hydrogen atoms result. Hydrogen gas is evolved.

The SO_4^{--} ions travel to the anode, give up their negative charges, and become plain sulphate radicals. Now SO_4 does not stand for any known substance: the group cannot exist alone, and it immediately takes hydrogen from the water and liberates oxygen:

$$SO_4 + H_2O = H_2SO_4 + O.$$

Each two atoms of oxygen formed unite to form a molecule, and the gas is evolved at the anode.

Thus it is seen that when water containing sulphuric acid is electrolysed, hydrogen and oxygen are given off,

and although these gases come from the sulphuric acid, they are immediately replaced by hydrogen and oxygen from the water, and the amount of acid in the solution remains constant. The effect is as though the water itself were electrolysed.

Electrolysis of copper sulphate solution, using platinum electrodes

The copper sulphate dissociates:

$$CuSO_4 \rightarrow Cu^{++} + SO_4^{--}.$$

(Note that the copper, being bivalent, has two units of charge for its ion, as has the SO_4^{--} ion.)

When electricity passes through the solution, copper ions travel to the cathode, give up their charges, and are deposited as metallic copper. The sulphate ions travel to the anode, give up their charge, and react with water molecules as in the case of sulphuric acid previously described, and oxygen is evolved.

So, using platinum electrodes, the effect of electrolysing copper sulphate solution is to deposit copper at the cathode and liberate oxygen at the anode.

Electrolysis of copper sulphate solution, using copper electrodes

The copper ions travel to the cathode as in the previous case, and are deposited.

The sulphate ions, having given up their charge at the anode and become uncharged sulphate radicals, are now in close proximity to copper atoms (on the copper anode). They have a greater chemical affinity for these copper atoms than for the hydrogen atoms of the water, and so combine with them:

$$SO_4 + Cu = CuSO_4.$$

The copper sulphate molecules so formed disperse into the solution. Thus the concentration of the copper

sulphate is kept up, and the net result is that copper is deposited on the cathode and (the same amount) dissolved from the anode. This principle is used in copper refining and copper-plating.

Electroplating

The metallic object to be plated is made thoroughly clean and given a matt surface. It is then placed as cathode in a solution of a salt of the metal which is to be deposited. The anode is a plate of this metal.

The best results for copper-plating of iron are obtained with a solution of copper sodium tartrate.

Silver is generally deposited from a solution of silver potassium cyanide together with excess of potassium cyanide. The electrolyte used for gold-plating is gold potassium cyanide, and for nickel-plating, nickel ammonium sulphate. In the latter case the metal is generally first copper-plated and the nickel then deposited on the copper.

Chromium is plated on iron and steel by electrolysis of a solution of chromium trioxide together with a small amount of chromium sulphate.

Electrotyping

Copies of type which has been set up are made to save wear and tear of the type and also to avoid resetting the type or keeping it standing for later editions of books.

A wax cast of the type is made, and this is dusted with powdered graphite, a form of carbon which is a good conductor of electricity. This is immersed in copper sulphate solution and copper is deposited on the graphite, a copper anode being used. A copper deposit of one-sixteenth of an inch is obtained, and this is removed. Suitably backed with soft metal (type metal) and mounted, it produces perfect copies of the type.

Statues, medals, woodcuts, etc., can be reproduced faithfully by this method. A reverse of the object is

made in gutta-percha, dusted with graphite powder, and copper-plated. The copper coating is removed, and, suitably backed, may be used to cast further reproductions.

Electrolytic manufacturing processes

Many metals are prepared or refined by electrolysis of fused compounds or solutions of salts of the metals. These will be described under the headings of the metals concerned.

QUESTIONS

1. Explain what is meant by the terms: *electrolysis, electrolyte, voltameter, electrode, anode, cathode.*

2. State Faraday's laws of electrolysis.

3. Write an account of the electrolysis of copper sulphate solution, using (*a*) platinum electrodes, (*b*) copper electrodes.

4. Explain how the equivalent of a metal can be measured by means of electrolysis of one of its salts.

5. Write an account of the ionic hypothesis.

6. Write an account of the commercial applications of electrolysis.

CHAPTER XI

SOLUTION AND CRYSTALLIZATION

Solution

If some crystals of copper sulphate are shaken up with water, it is seen that the solid soon disappears and a homogeneous clear blue liquid is formed. The copper sulphate is dissolved in the water. The clear blue liquid is called a **solution** of copper sulphate in water. The substance dissolved, in this case copper sulphate, is called the **solute.** The liquid in which the solute is dissolved is called the **solvent.**

If more and more copper sulphate crystals are added and shaken up, they will continue to dissolve until a definite amount of solid is in solution, after which further addition of copper sulphate will result merely in the excess solid remaining undissolved at the bottom of the solution. Such a solution is said to be **saturated.**

If the above saturated solution, together with the excess solid, is heated gently, it will be noticed that more of the crystals dissolve as the temperature is raised, until perhaps it has all dissolved and the solvent could dissolve more. The solution is now no longer saturated, and so at this higher temperature a saturated solution will contain more solute dissolved in the same amount of solvent than is possible at the lower temperature. It is seen, then, that in order to express the solubility of a substance in any particular solvent, the temperature must be stated.

Solubility. — *The solubility of a substance in a given solvent at a given temperature is the mass of that substance that will dissolve in* 100 *gm. of the solvent in the presence of excess of the solute.*

Solubility Curves

It is convenient to express the solubility of a substance graphically by means of solubility curves, the horizontal axis of the curves measuring the temperature and the vertical axis the solubility, the latter being expressed as grammes of the solute per 100 gm. of solvent (fig. 15).

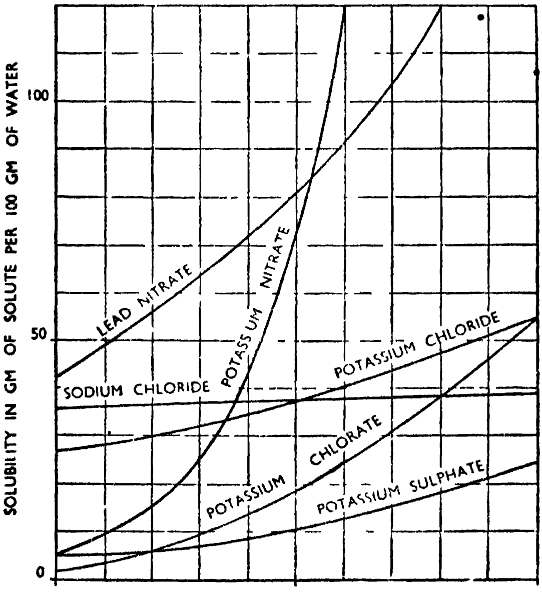


Fig. 15. — Solubility Curves of some Salts

It is seen from these curves that the solubility increases regularly with rise in temperature. Also it is seen that both the solubility and the rate of increase of solubility with rise of temperature are different for different salts. With certain salts, however, there is observed a decrease in solubility with rise in temperature, but the

general rule is: increase in solubility with rise in temperature.

Determination of the solubility of a salt in water at a certain temperature

Into a beaker pour about 50 c.c. of distilled water and add some of the salt. Stir and warm to increase the rate at which the salt dissolves, adding more of the salt, as necessary, so that at about 10° above the required temperature there is some excess of the solute at the bottom. Stop stirring and allow it to cool to this temperature. As soon as the required temperature has been reached, quickly but carefully decant a portion of the *clear* solution into a weighed evaporating basin and weigh again. Evaporate to dryness on a steam bath, allow the evaporating basin to cool, and weigh again. The results are calculated as follows:

Solubility of potassium chlorate in water at 50° C.

Weight of evaporating basin = 15·31 gm.
Weight of evaporating basin + solution = 72·43 gm.
Weight of evaporating basin + potassium chlorate
= 24·83 gm.
Weight of water in solution = 72·43 – 24·83 = 47·60 gm.
Weight of potassium chlorate in this solution
= 24·83 – 15·31 = 9·52 gm.

i.e. at 50° C.,

47·60 gm. of water dissolve 9·52 gm. potassium chlorate.

$\therefore$ 1 ,, ,, $\dfrac{9 \cdot 52}{47 \cdot 60}$,, ,,

and 100 ,, ,, $\dfrac{9 \cdot 52 \times 100}{47 \cdot 60}$,, ,,

= 20·0 gm. potassium chlorate.

i.e. *The solubility of potassium chlorate is* 20 *gm. per* 100 *gm. of water at* 50° *C.*

Solvents other than water

While water is the commonest and most important of solvents, there are many others used to a great extent in everyday life, a few of which may be mentioned.

Alcohol dissolves resins and many other substances. A solution of iodine, itself a solid, in alcohol is called **tincture of iodine**, and is used for cuts and bruises. **Methylated spirit** is mostly ethyl alcohol (there are a large number of alcohols; ethyl alcohol is the ordinary one which is present in beer, wines, and spirits), but it also contains another alcohol, methyl alcohol, and some colouring matter and other substances. These additions make it distinctive and unpleasant, and render it exempt from the duty put on alcohol used for drinking purposes.

Petrol and **benzene** dissolve grease and so are used for cleaning clothes, etc. They also dissolve rubber, making the rubber solution used for repairing punctures.

Ether dissolves oils, fats, and resins, and so is a very useful solvent. Great care must be observed not to have a naked flame near ether, as it is extremely inflammable.

Supersaturation

It is found that in some cases a hot saturated solution, free from solid, can be cooled without crystals depositing, even though the solubility curve shows that the solubility decreases with fall in temperature. It seems, then, that under certain conditions a solution may contain more solute than is necessary to form a saturated solution. Such a solution is said to be **supersaturated.** A supersaturated solution cannot exist in the presence of solid solute, and therefore if a crystal of the solute is added to such a solution, the excess solute will at once be precipitated. This explains why we put the phrase "in the presence of excess of the solute" in our definition of solubility.

Supersaturation may be readily demonstrated in the case of sodium thiosulphate (photographers' "hypo"). Place a little water in the bottom of a boiling tube, and add crystals of sodium thiosulphate until the tube is nearly full. Heat gently until all the crystals have dissolved. On cooling, keeping the tube vertical and still, the contents will remain liquid: we have a supersaturated solution. Now add a single small crystal to the solution. Immediately crystallization commences, starting from the top and spreading downwards, until nearly the whole contents of the tube are crystals. The little remaining liquid at the bottom is a saturated solution. It will be observed that heat is given out as precipitation takes place.

Water of crystallization

Place some crystals of copper sulphate in a test-tube fitted with a rubber stopper and right-angled delivery

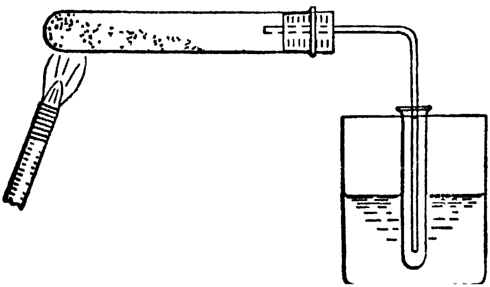


Fig. 16

tube leading to another test-tube surrounded by cold water in a beaker (fig. 16).

On heating the crystals gently, a colourless liquid is seen to condense in the vertical test-tube, and the blue crystals in the other tube turn to a white powder. The liquid collected is found to be water.

The same result is obtained if the experiment is

repeated with certain other substances, for example, sodium carbonate (washing soda), ferrous sulphate, and sodium sulphate crystals. The powder left after driving the water off is **anhydrous** (i.e. without water) copper sulphate. The water was combined with it to form the crystals.

Water which combines with a substance causing that substance to form crystals is called **water of hydration, or water of crystallization.** The compound of a substance with water is called a **hydrate,** and it is found that a definite number of molecules of anhydrous substance combine with a definite number of molecules of water to form the hydrate:

$$\text{e.g. } CuSO_4 + 5H_2O = CuSO_4{\cdot}5H_2O.$$

Some substances form more than one hydrate. We shall come across various examples of this later.

It was noted that whereas hydrated copper sulphate is blue, the anhydrous salt is white. As soon as the white powder comes into contact with water the blue colour of the hydrated salt is observed. This colour change affords a good test for water, as we shall see. Anhydrous copper sulphate is used to test shooting boots for water-tightness.

It is to be noted that not all crystalline substances contain water of hydration. Some common salts which do not are: sodium chloride, potassium chloride, potassium nitrate, potassium chlorate, and ammonium sulphate.

Efflorescence and deliquescence

Some substances lose all or part of their water of crystallization when merely exposed to the air. This is known as **efflorescence.** For example, it is well known that crystals of washing soda become coated with a white powder. This powder is a lower hydrate than the large crystals, containing only one molecule of water of

hydration to one molecule of sodium carbonate, whereas the crystals contain ten:

$$Na_2CO_3{\cdot}10H_2O = Na_2CO_3{\cdot}H_2O + 9H_2O.$$

Certain substances are found to absorb moisture from the air, and are said to be **hygroscopic.** In some cases the water absorbed dissolves the substance, forming a saturated solution. These substances are said to be **deliquescent,** and the absorption of water vapour from the air to form a saturated solution is called **deliquescence.** Common examples of deliquescent substances are calcium chloride and sodium hydroxide. These substances should be kept in airtight containers.

It is to be noted that some hygroscopic substances absorb water but do not make a solution. Such substances are not deliquescent. An example of this is quicklime, CaO. This absorbs water from the air, making slaked lime, $Ca(OH)_2$, a white powder which remains dry.

QUESTIONS

1. Explain the terms: *solution, solvent, solute, saturated solution, solubility.*

2. Describe how you would measure the solubility of potassium nitrate at the temperature of the laboratory.

3. What is meant by a *supersaturated solution*? Describe how you would demonstrate the phenomenon of supersaturation.

4. What is meant by *water of hydration*? How would you ascertain if a certain crystalline substance contained water of hydration or not?

5. How would you measure the percentage of water of hydration in copper sulphate crystals?

6. Calculate the percentage of water of hydration in washing soda crystals, $Na_2CO_3{\cdot}10H_2O$.

7. Explain what is meant by the terms *deliquescence* and *efflorescence.* Distinguish between deliquescent substances and hygroscopic substances.

CHAPTER XII

THE AIR: OXYGEN

Animals and plants need air in order to live. You know that you are constantly using air in your breathing, and you have experienced discomfort and headache when too many people have been for some time in a badly ventilated room. Fishes get their air from the water, because air dissolves to a sufficient extent in the water and they have the means of extracting it for their own use.

Substances need air in which to burn. You have noticed, no doubt, that a coke or anthracite stove burns fiercely when the air inlet at the bottom is well open, but slows down and finally goes out if it is closed. You could not possibly live in a gasometer full of gas, but if you could by some means enable yourself to do so you would be able to sit on the bottom with gas all around and strike matches to your heart's content. They would not be able to burn, because there is no air there. The gas could not burn, for the same reason.

Air, then, is necessary for combustion. Note that the term *combustion* includes other processes than what is generally meant by burning. For example, the rusting of iron and the tarnishing of metals are cases of combustion, and can take place only when air is present.

Examination of the combustion of magnesium. — Place about six inches of magnesium ribbon in a weighed crucible (with lid) and weigh again. Heat gently with the lid off until the magnesium begins to burn, and then take away the Bunsen burner and place the lid on the crucible. When the bright light dies down,

open the lid a little, using crucible tongs. It will be noticed that as more air gets in the burning continues more fiercely. When this no longer happens, heat again until all the magnesium is burnt, allow it to cool, and weigh again.

A *gain* in weight is observed. That is, the white ash weighs more than the metal before it was burnt. This experiment may be repeated using copper instead of magnesium. There is no flame in this combustion, but the same result is obtained: the black copper ash weighs more than the metal before it was burnt.

What about a piece of wood, or a candle? Our everyday observation indicates that these do not weigh more after burning than before. Yet the answer is: Yes, they do, but some of the products, being volatile, disappear into the air. You can smell some of them, and observe the soot. But if they are collected by something that will absorb them, it will be found that the products of the burnt candle and wood weigh more than the original substances.

Our next question is: where does this extra matter come from? The most obvious guess is: the air. This is correct.

Place a small piece of phosphorus in a deflagrating spoon, warm it until it begins to burn, and plunge it into a bell jar standing in a trough of water (fig. 17). The phosphorus burns for a time, giving off dense white fumes. Soon the flame dies down and goes out. The water in the trough is seen to have risen up the bell jar. Measurement shows that approximately $\frac{1}{5}$ of the air has been used up. On withdrawing the phosphorus into fresh air, it immediately starts to burn again. Let it finish in the fume cupboard.

This experiment may be repeated without igniting the phosphorus first. It burns slowly without a flame, and after a few days the burning will have stopped and $\frac{1}{5}$ of the air will have been used up.

Iron may be rusted in an enclosed space of air by

wetting the inside of a gas jar with water, sprinkling iron filings inside so that they stick, and inverting over a trough of water. Again, after a few days it is seen that about $\frac{1}{5}$ of the air has been used up, and the remaining $\frac{4}{5}$ will not allow anything to burn in it.

It is clear, then, that air is necessary for combustion, that $\frac{1}{5}$ of the air is used up when combustion takes place, and that it is the weight of this part of the air that causes the increase in weight of the substance burnt. The remaining $\frac{4}{5}$ of the air will not support combustion.

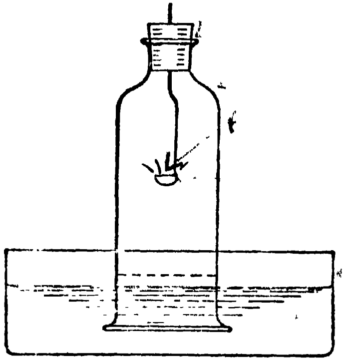


Fig. 17

The active part of the air, necessary for burning and supporting life, and used up when doing so, is called *oxygen*. The remaining inactive part of the air is mostly a gas called *nitrogen*.

OXYGEN

Occurrence

Oxygen occurs in the uncombined state in the air to the extent of 21 per cent by volume, or 23 per cent by weight. Combined, it occurs in the earth to a very large extent, very nearly half the weight of the earth's crust being due to oxygen. Among the thousands of oxygen

compounds occurring naturally water may be mentioned, and 89 per cent by weight of water is oxygen.

History

Oxygen was first prepared by the Swedish chemist Scheele in 1772. It was also discovered independently by Priestley in 1774. Priestley prepared his oxygen by heating mercuric oxide.

Laboratory preparation

Oxygen is generally prepared in the laboratory from potassium chlorate, using manganese dioxide as a catalyst.

Potassium chlorate crystals are crushed in a mortar and mixed with about ¼ of their weight of manganese dioxide.

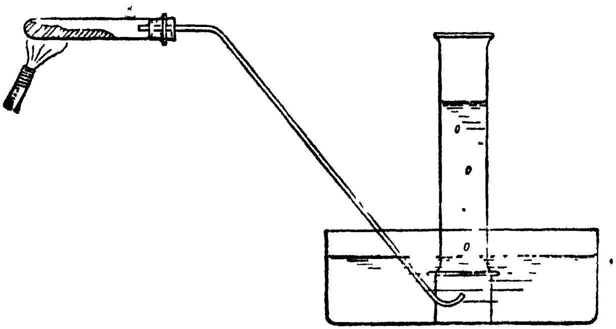


Fig. 18. — Preparation of Oxygen from Potassium Chlorate

This mixture is often referred to as " oxygen mixture ", and a supply ready mixed is sometimes kept in the laboratory. Some of the mixture is placed in a hard glass test-tube held horizontally and fitted with delivery tubing (fig. 18). The gas is collected over water.

On heating, the potassium chlorate decomposes into potassium chloride and oxygen:

$$2KClO_3 = 2KCl + 3O_2.$$

The manganese dioxide, as has been said, behaves as a catalyst, in that it increases the speed of the reaction at a given temperature. This has the effect of enabling the process to take place rapidly at a lower temperature than is possible without the manganese dioxide. The latter is left unchanged after the reaction.

Another method used in the laboratory for the preparation of oxygen is by adding water to sodium peroxide.

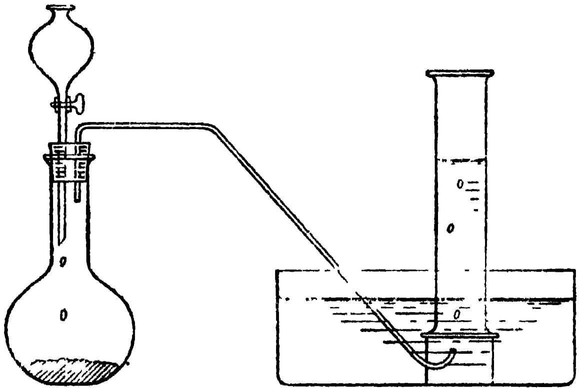


Fig. 19. — Preparation of Oxygen from Sodium Peroxide

oxide. Sodium hydroxide is formed in addition to the oxygen. This method is convenient and has the advantage of giving oxygen of a high degree of purity. The water is allowed to drip on to the sodium peroxide from a dropping funnel, that is, a funnel fitted with a tap, so that the rate at which the water drips through can be controlled (fig. 19). Thus the rate at which the oxygen is evolved can be controlled. No heating is necessary.

$$\underset{\text{(sodium peroxide)}}{2Na_2O_2} + 2H_2O = \underset{\text{(sodium hydroxide)}}{4NaOH} + O_2.$$

Other methods by which oxygen may be prepared are:

(*a*) By heating mercuric oxide in a hard glass test-tube. Oxygen and mercury are the products, the mercury vaporizing and condensing as a mirror on the upper, cooler part of the test-tube.

(*b*) By heating higher oxides of certain metals, for example, red lead or manganese dioxide. Oxygen is evolved and a lower oxide formed:

$$\underset{\text{(red lead)}}{2Pb_3O_4} = \underset{\text{(litharge)}}{6PbO} + O_2.$$

(*c*) By heating certain other compounds rich in oxygen. One example (potassium chlorate) we have discussed. Others are potassium nitrate and sodium nitrate, the nitrite being formed in each case:

$$\underset{\text{(potassium nitrate)}}{2KNO_3} = \underset{\text{(potassium nitrite)}}{2KNO_2} + O_2.$$

Industrial preparation

The two commonest substances containing oxygen are air and water, and so it would seem that the gas might be prepared on a large scale from either. This is, in fact, the case.

Preparation from air. — Air is first liquefied by allowing compressed air to expand through a valve. This cools the air, which is made to circulate again and is recompressed and again forced through the valve, when it is cooled still more. The cold air, returning from the valve to be recompressed, is made to cool still further the air approaching the valve. Finally, the cooling is sufficient to liquefy the air, and liquid air collects below the valve.

Since air is a *mixture* and not a compound, its constituent substances boil at different temperatures. The boiling-point of nitrogen is $-195°$ C. and that of oxygen $-182°$ C. Hence, on allowing liquid air to boil, the first gas given off will be largely nitrogen, the liquid left being

a mixture which is mostly oxygen. The process has been perfected so that almost pure oxygen is obtained.

The gas is compressed at 120 atmospheres into steel cylinders for transport and use.

Preparation from water. — Although most of the oxygen used commercially is made from air, it is also prepared as a by-product in the preparation of hydrogen by the electrolysis of water. The oxygen produced by this means is, like the hydrogen, very pure.

Properties of oxygen

Oxygen is a colourless, odourless gas slightly denser than air. It is soluble to a small extent in water. On cooling it liquefies to a bluish liquid.

Oxygen will not burn, but it supports combustion, and this is its most important property. Substances which burn in air do so much more readily in oxygen. For example, a glowing splint of wood is rekindled when plunged into a jar of oxygen. Many metals and non-metals burn in oxygen, forming oxides.

Burning of non-metals in oxygen

(*a*) **Phosphorus.** — A small piece of yellow phosphorus is warmed in a deflagrating spoon. As soon as it begins to burn, it is plunged into a jar of oxygen. The phosphorus burns brilliantly and dense white fumes are produced. When the burning has subsided, the spoon is removed and the contents of the jar shaken up with a little water. The fumes dissolve. The solution is tested with blue litmus paper. It is immediately turned red, showing that the solution is an acid:

$$4P + 5O_2 = \underset{\text{(phosphorus pentoxide)}}{2P_2O_5}.$$

$$P_2O_5 + 3H_2O = \underset{\text{(phosphoric acid)}}{2H_3PO_4}.$$

(*b*) **Sulphur.** — A similar experiment may be performed with sulphur. The sulphur burns with a beautiful violet flame, and the misty fumes of sulphur dioxide formed dissolve in water, forming an acid, sulphurous acid:

$$S + O_2 = \underset{\text{(sulphur dioxide)}}{SO_2}.$$

$$SO_2 + H_2O = \underset{\text{(sulphurous acid)}}{H_2SO_3}.$$

(*c*) **Carbon.** — A piece of charcoal is heated in a deflagrating spoon until it glows, and is quickly plunged into a jar of oxygen. It glows brightly in the gas, forming carbon dioxide, a colourless gas. On shaking up with water, some of the gas will dissolve, and the solution is found to turn blue litmus paper slowly dull red. The solution is carbonic acid:

$$C + O_2 = \underset{\text{(carbon dioxide)}}{CO_2}.$$

$$CO_2 + H_2O = \underset{\text{(carbonic acid)}}{H_2CO_3}.$$

Burning of metals in oxygen

(*a*) **Sodium.** — A small piece of sodium is heated in a deflagrating spoon, and as soon as it begins to burn is plunged into a jar of oxygen. It burns very brightly, giving off yellowish-white fumes of sodium peroxide. These fumes dissolve when shaken up with water, and the solution is found to turn red litmus paper blue. This is due to the formation of sodium hydroxide, an alkali:

$$2Na + O_2 = \underset{\text{(sodium peroxide)}}{Na_2O_2}.$$

$$2Na_2O_2 + 2H_2O = O_2 + \underset{\text{(sodium hydroxide)}}{4NaOH}.$$

(*b*) **Magnesium.** — This metal burns brightly in oxygen as it does in air, and the white fumes of magnesium oxide formed dissolve to some extent in water, giving magnesium hydroxide, an alkali:

$$\underset{}{2Mg + O_2} = \underset{\substack{\text{(magnesium}\\\text{oxide)}}}{2MgO}.$$

$$MgO + H_2O = \underset{\substack{\text{(magnesium}\\\text{hydroxide)}}}{Mg(OH)_2}.$$

(*c*) **Iron.** — A piece of iron wire is twisted on to the bottom of a deflagrating spoon and the end of the wire is dipped into molten sulphur. The sulphur is lit, and the spoon is plunged into a jar of oxygen. The burning sulphur heats the iron till it burns in the oxygen, emitting bright sparks and forming a molten globule of black oxide of iron, triferric tetroxide:

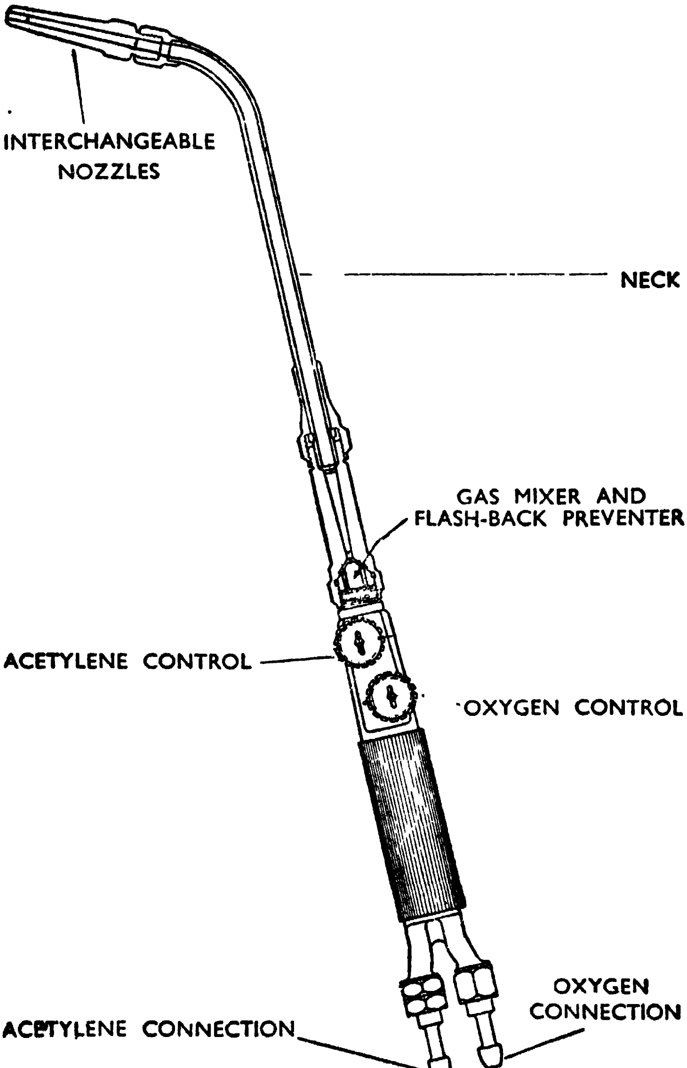
$$3Fe + 2O_2 = \underset{\substack{\text{(triferric}\\\text{tetroxide)}}}{Fe_3O_4}.$$

This oxide does not dissolve in water.

It is seen from the above examples of reactions of metals and non-metals with oxygen that the non-metals form oxides which dissolve in water to form acids, and the metals form oxides which are either insoluble or dissolve in water to form alkalis. The former are called **acidic oxides, and the latter basic oxides.**

Uses of oxygen

We have seen that substances which burn in air do so much more fiercely in oxygen. This fact gives rise to the chief use of oxygen, namely, in the oxy-acetylene flame for cutting and welding steel (fig. 20). In this flame, where a jet of acetylene is fed with a supply of oxygen; temperatures as high as 4000° C. can be obtained. Other



(By Courtesy of British Oxygen Co., Ltd.)

Fig. 20. — Oxy-acetylene Blow-pipe

gases, such as hydrogen and propane, are used instead of acetylene for certain purposes.

Oxygen is used in flying as an aid to breathing at high altitudes. It is also used by doctors when a patient is given an anæsthetic, and generally to assist breathing in certain illnesses.

Ozone (O_3)

Ozone is prepared by the passage of a silent electric discharge through oxygen. This can conveniently be

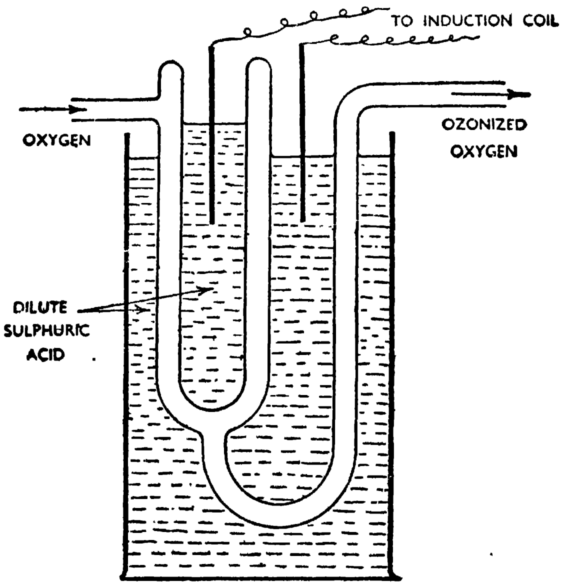


Fig. 21. — Preparation of Ozone

done by means of the apparatus shown in fig. 21. This consists of a double glass tube, oxygen being passed slowly through the space between the inner and outer walls. The inner tube and the vessel in which the apparatus stands contain dilute sulphuric acid, and platinum

leads dipping in these are connected to the terminals of an induction coil. The silent electrical discharge passing through the oxygen from one quantity of acid to the other causes partial conversion of the oxygen to ozone. The mixture of oxygen and ozone emerging is called ozonized oxygen.

Properties of ozone

Ozone is a colourless gas with a pungent smell suggestive of chlorine. Even small quantities of ozone in oxygen can be smelt distinctly.

It is a powerful oxidizing agent. It liberates iodine from potassium iodide:

$$2KI + H_2O + O_3 = 2KOH + O_2 + I_2.$$

Lead sulphide is oxidized to lead sulphate:

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

Sulphur dioxide is oxidized to sulphur trioxide:

$$SO_2 + O_3 = SO_3 + O_2.$$

Ozone causes mercury to lose its mobility; its surface darkens and it " wets " glass. This may be due to surface oxidation.

Uses of ozone

Ozone is used to sterilize water and air. It is also used for bleaching some oils.

Formula of ozone

When ozone decomposes, two volumes of ozone form three volumes of oxygen;

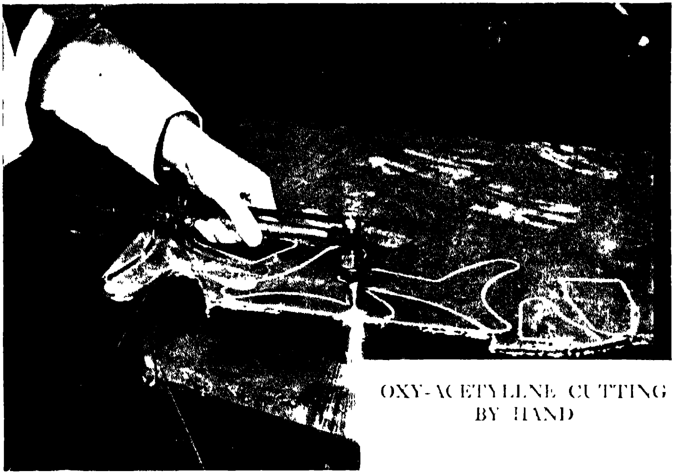
∴ by Avogadro's hypothesis, two *molecules* of ozone form three *molecules* of oxygen.

But 3 molecules of oxygen contain 6 atoms.

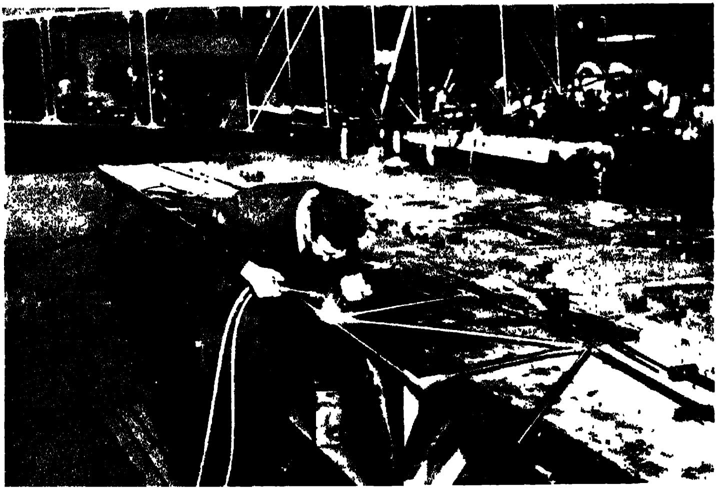
∴ 2 molecules of ozone contain 6 atoms.

∴ 1 molecule of ozone contain 3 atoms.

The formula for ozone, therefore, is O_3.



OXY-ACETYLENE CUTTING BY HAND



(Photographs by courtesy of the British Oxygen Co., Ltd.)

OXY-ACETYLENE WELDING OF AEROPLANE PARTS

Allotropy

This phenomenon of an element existing, as oxygen does, in more than one form, those forms having different physical, and often chemical, properties, is known as **allotropy.** Ozone is said to be an **allotrope** of oxygen. (See allotropy of sulphur, phosphorus, and carbon, pp. 175, 194, 203.)

THE PHLOGISTON THEORY

One of the most important advances in the history of chemistry was made in connection with combustion. Here is a brief account of it.

A German chemist named Stahl (1660–1734) propounded his **Phlogiston Theory** in explanation of the fact of combustion. He said that all combustible substances contain a principle of combustibility, to which he gave the name *phlogiston.* When a substance burns, this phlogiston escapes, air being a good absorber of phlogiston. The ash, or *calx,* as it was called, is left behind, and consists of the substance minus its phlogiston. Thus a metal was considered to be a compound of calx and phlogiston.

Charcoal burns leaving very little ash, and so was considered to be very nearly pure phlogiston. Then, if the calx of a metal was heated with carbon, it would absorb the necessary phlogiston to convert it into the metal. The metal is indeed formed, although for a reason entirely different from that given by the phlogistonists.

One great difficulty with which the phlogiston theory had to contend was that it was found that the calx of a metal, as we saw in the case of magnesium, is heavier than the metal itself. The supporters of the theory explained that phlogiston was the principle of levity as well as combustibility, and, in fact, helped to support the metal in air. When this principle of levity was

removed, the resulting calx had lost its support and was consequently heavier.

Strange as it may seem to us now, the phlogiston theory received universal support for many years. Its overthrowal was due to the industry and logical reasoning of the brilliant French chemist, **Lavoisier** (1743–94).

Priestley, who, as we have said, discovered oxygen in 1774, mentioned this fact in the same year to Lavoisier in Paris. Lavoisier realized the importance of Priestley's discovery, judging that this gas was the portion of the

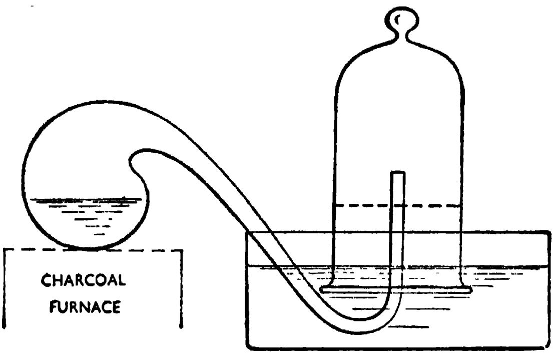


Fig. 22. — Lavoisier's 12-day Experiment

air that combined with the metal during its combustion to produce the calx. His famous quantitative experiment to prove this was, briefly, as follows.

A weighed amount of mercury was heated in a clay retort over a charcoal furnace for 12 days, at a temperature just below the boiling-point of the mercury. The open end of the retort led to an enclosed volume of air in a bell jar over mercury, as is shown in fig. 22. By this time there was no further change in the volume of the air in the bell jar, and Lavoisier found that combustion of some of the mercury had taken place, forming 45 grains of the red calx on the surface of the mercury in the retort. The volume of air in the bell jar had

diminished by 8 c. in. The gas left in the bell jar would not support combustion or life.

He now collected the 45 grains of calx of mercury and heated it, as Priestley had done, and collected the oxygen.

Lavoisier found that:

(1) 41 grains of mercury were formed from the calx, making up the original amount of mercury started with.

(2) 8 c. in. of oxygen were evolved from the calx of mercury, making up the loss in volume of the air due to the combustion of the mercury.

(3) This oxygen supported burning and life vigorously, and, added to the residual air in the bell jar, made ordinary air.

Lavoisier, by this and many other experiments, proved that when combustion of a metal takes place, it uses up part of the air, oxygen, combining with it to form the calx, or oxide. The remainder of the air, mostly nitrogen, takes no part in the combustion, merely diluting the oxygen and making the process less vigorous.

Lavoisier gave the name **oxygen** (meaning acid-former) to Priestley's gas, because he found that the oxides of certain non-metals dissolve in water, forming acids, and he assumed that it was the oxygen that caused the acidity. We know now, of course, that he was wrong, because oxides of metals do not give acids, and some acids do not contain oxygen.

Priestley, whose discovery of oxygen was the immediate cause of Lavoisier's experiments which overthrew the phlogiston theory, himself remained all his life an ardent supporter of that theory. He called oxygen "dephlogisticated air".

QUESTIONS

1. Describe the laboratory preparation of oxygen.

2. What weight of potassium chlorate is necessary to prepare 500 c.c. of oxygen at S.T.P.?

3. Write an account of experiments you would perform to illustrate the properties of oxygen.

4. How is oxygen prepared commercially?

5. Write an account of the uses of oxygen.

6. What is meant by *combustion*? Give examples.

7. Write an account of the phlogiston theory of combustion.

8. Describe Lavoisier's experiments and explain how his results led to the overthrowal of the phlogiston theory.

9. Describe how you could obtain ozonized oxygen. What are its principal properties? What evidence is there that ozone is an allotrope of oxygen, and that its formula is O_3?

CHAPTER XIII

HYDROGEN: WATER

Occurrence

Hydrogen occurs in the free state to a very small extent on the earth, but to a large extent in the sun and other stars. Combined, it occurs in large quantity in thousands of compounds; for example, in water and oils. Compounds of hydrogen are present to a large extent in all animals and vegetables.

History

Hydrogen was first prepared and carefully investigated by **Cavendish** in 1766, by the action of dilute sulphuric acid on iron, although the gas had probably been previously obtained by Van Helmont and Boyle.

Laboratory preparation

The usual method of preparing hydrogen in the laboratory is by the action of zinc and dilute sulphuric acid.

The zinc granules are placed in a Woulfe bottle fitted with a thistle funnel and delivery tubing which leads to a gas jar inverted over water (fig. 23). When dilute sulphuric acid is poured down the funnel, hydrogen is evolved, zinc sulphate solution being left in the bottle:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Although the above is the most usual laboratory method for the preparation of hydrogen, the gas can also be prepared by the action of various metals and

dilute hydrochloric or sulphuric acid; for example, magnesium, iron, and aluminium:

$$Mg + H_2SO_4 = MgSO_4 + H_2.$$
$$Mg + 2HCl = MgCl_2 + H_2.$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$
$$Fe + 2HCl = FeCl_2 + H_2.$$
$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2.$$
$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

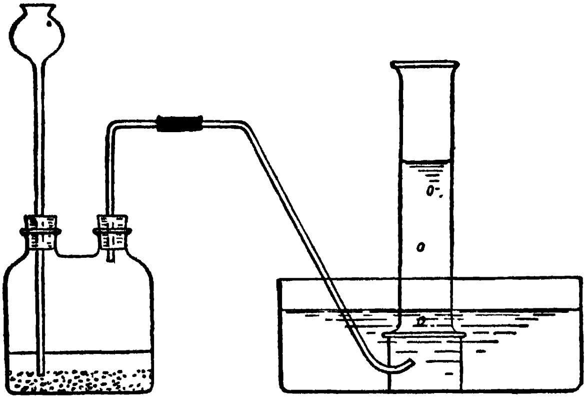


Fig. 23. — Preparation of Hydrogen

Hydrogen is also liberated from nitric acid by magnesium, if the acid is *very* dilute. A few drops of ordinary laboratory dilute nitric acid to half a test-tube of water will give the requisite dilution.

$$Mg + 2HNO_3 = Mg(NO_3)_2 + H_2.$$

Potassium, sodium, and calcium will liberate hydrogen from cold water:

$$2K + 2H_2O = 2KOH + H_2.$$
$$2Na + 2H_2O = 2NaOH + H_2.$$
$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

formed. -- Hydrogen is prepared from zinc and dilute sulphuric acid in a Woulfe bottle (fig. 24), and dried by passing it through a U-tube containing lumps of calcium chloride. This leads to a jet from which the gas is burnt. A convenient jet can be made by attaching a blowpipe to the gas-delivery tubing; this overcomes the disadvantage of a glass jet, which melts at the tip and closes up.

Before the gas is lit, it must be tested to make sure that there is no air with it, or a dangerous explosion may

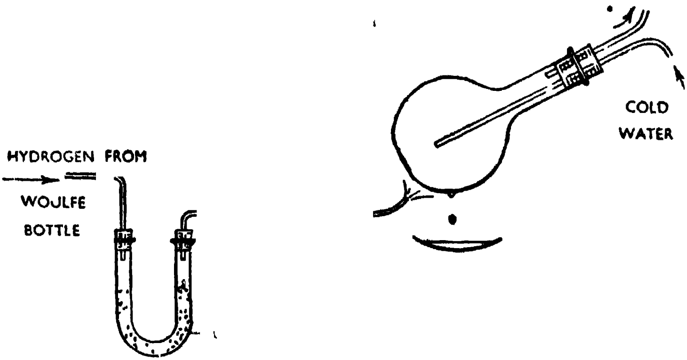


Fig 24. — Formation of Water by burning Hydrogen

occur. To do this, hold a test-tube over the jet for a few seconds and test the gas collected with a lighted splint. A squeaky " pop " indicates a mixture of gas and air; quiet burning indicates hydrogen free from air and safe to light at the jet.

The hydrogen flame is allowed to impinge on to a cold surface, provided by a round-bottomed flask through which cold water is passed. Very soon drops of a colourless liquid are seen to collect on the cold surface, and these may be collected on a watch glass placed below.

The liquid is shown to be water by placing a drop on some anhydrous copper sulphate. The white powder is turned blue. (See Properties of Water, p. 115.)

Nascent hydrogen

The hydrogen molecule consists of two atoms, but when hydrogen is prepared, the atoms are liberated singly. They soon join up into pairs, however, to form molecules. The single atoms are much more active chemically than the molecules, and at the moment of liberation, hydrogen is found to take part in chemical changes with certain substances which do not occur when molecules of the gas are allowed to come into contact with those substances. Such hydrogen is called *nascent*, meaning " newly born ".

Atomic hydrogen is also formed when the gas is passed through an electric arc.

Uses of hydrogen

Hydrogen is used for the manufacture of ammonia, as a fuel (coal gas and water gas each contain hydrogen), in the hardening of oils to produce fats (for example, margarine), in the " hydrogenation " of coal to produce oils, for the oxy-hydrogen blowpipe, and to fill balloons.

Atomic hydrogen is used for welding. The gas is passed through an electric arc between tungsten electrodes, when a proportion of hydrogen molecules split up into atoms. Just beyond the arc these atoms combine again to form molecules, and in doing so give out a large amount of heat. The extremely high temperature reached, the high rate at which the heat can be applied to a surface, and the fact that oxidation cannot take place, all make the atomic hydrogen flame very efficient for welding, particularly for difficult alloys, e.g. those containing chromium, manganese, tungsten, and aluminium.

WATER, H_2O

Occurrence

Sea water is about 96 per cent pure water, numerous salts being in solution, the most common of which is sodium chloride.

Spring and river water are purer than sea water, the substances in solution depending upon the locality. In many natural waters calcium and magnesium salts are present, and these cause what is known as *hardness* in the water. There is also a varying quantity of solid matter in suspension in river water.

Rain water is very nearly pure. A small amount of gaseous matter is found in solution, and dust and other matter from dirty air are found dissolved and in suspension in town rain water.

Distilled water. — This is the purest water in use, except in very particular cases. It contains a small amount of gaseous matter in solution, and also a very small quantity of glass or metal dissolved from the distilling apparatus. This is negligible for ordinary use (e.g. storage cells) and experimental work, but for measurements of conductivity of solutions it is not good enough, and specially pure water — "conductivity water" — has to be prepared. This is done by a difficult and lengthy process; conductivity water is expensive.

Properties

Water is a colourless, odourless liquid, boiling at 100° C., and freezing at 0° C. It has a density of 1 gm. per cubic centimetre, and its refractive index is 1·333.

Water turns white anhydrous copper sulphate blue, causing the formation of the hydrated salt, $CuSO_4{\cdot}5H_2O$. This is used as a test for water, but it must be borne in mind that the colour change to blue only indicates that water is present, not that the substance is pure water. To ascertain that the substance is pure water, one or more of the above physical properties is measured, for example, the refractive index. It is often advantageous to choose this property for testing because the measurement can be made to a high degree of accuracy with a very small quantity of the liquid.

Water is, as we have seen, a common and useful

solvent. It combines, as water of crystallization, with certain salts to form hydrated salts.

Composition of water

Qualitative. — That water is a compound of hydrogen and oxygen is indicated, though not proved, by the fact that water is formed when dry hydrogen burns in air.

However, it can be shown that when pure hydrogen is burned in oxygen, water and nothing but water is formed. Similarly, a mixture of hydrogen and oxygen can be exploded and the product proved to be water only.

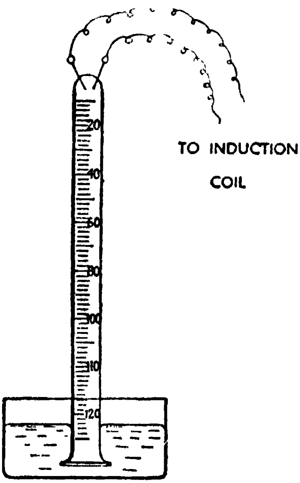


Fig. 25. — Volumetric Composition of Water — Eudiometer Method.

Quantitative — by volume. — This is best done by the eudiometer method.

A eudiometer is a graduated glass tube closed at one end, with two pieces of platinum wire fused into the closed end to make a spark gap. The eudiometer is filled with mercury and inverted over a vessel of mercury (fig. 25). Hydrogen is bubbled in, and the volume admitted is measured. Oxygen is then bubbled in and is similarly measured. A spark is allowed to cross the gap, by connecting the platinum wires to an induction coil. This causes the hydrogen and oxygen to combine with explosive violence, forming water.

On cooling, the volume of residual gas is measured. (The water formed, being a mistake on the inside wall of the vessel, has a negligible volume.) The gas left in the tube must be tested to see if it is hydrogen or oxygen.

If it relights a glowing splint of wood, it is oxygen; if it extinguishes a glowing splint, but burns when a lighted splint is applied, it is hydrogen. Thus the relative volumes of hydrogen and oxygen that have combined to form water can be deduced. The proportions are found to be 2 volumes of hydrogen to 1 volume of oxygen.

For example, if 50 c.c. of hydrogen and 50 c.c. of oxygen are delivered into the eudiometer, and after the explosion 25 c.c. of a gas which proves to be oxygen are left, then the water must have been formed from

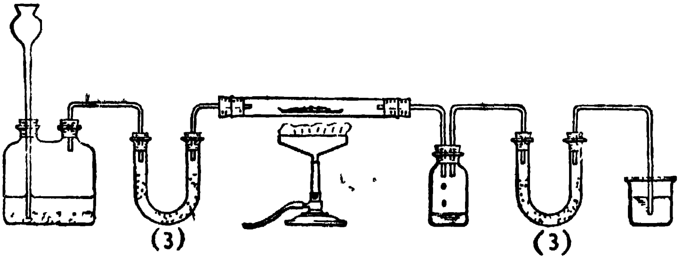


Fig. 26. — Gravimetric Composition of Water — Dumas' Method

50 c.c. of hydrogen and 25 c.c. of oxygen, that is, from 2 volumes of hydrogen and 1 volume of oxygen.

Quantitative — by weight. — This may be determined in the school laboratory by a simplification of the method originally used by Dumas.

Pure dry hydrogen is passed over heated copper oxide. Water is formed, and is collected and weighed:

$$H_2 + CuO = H_2O + Cu.$$

The hydrogen is generated from zinc and dilute sulphuric acid in a Woulfe bottle (fig. 26). The gas is passed through three U-tubes with calcium chloride. This dries the hydrogen, which is then passed over a weighed quantity of copper oxide in a porcelain boat, placed in a hard glass tube and heated strongly by a Bunsen burner fitted with a flame spreader. Some of the water formed drips

into the little bottle and the rest is absorbed in three more calcium chloride U-tubes. The unused hydrogen bubbles through mercury contained in a small beaker. This prevents moisture from the air being absorbed by the calcium chloride, and also provides an indication of the rate at which the hydrogen is passing through the apparatus.

The bottle and the three U-tubes on the right-hand side of the diagram are weighed before and after. The increase in weight recorded is, of course, the weight of water formed.

The loss in weight of the copper oxide in the porcelain boat is the weight of oxygen that has gone to make this water.

The difference between these two quantities must be the weight of hydrogen in the water.

For example, if the increase in weight of the calcium chloride tubes is 0·9 gm., and the loss in weight of the copper oxide is 0·8 gm., then

0·9 gm. of water contain 0·8 gm. of oxygen,

$\therefore$ weight of hydrogen in this water = 0·1 gm.,

i.e. 0·8 gm. of oxygen combine with 0·1 gm. of hydrogen to form 0·9 gm. of water.

Hence the gravimetric composition of water is 8 parts by weight of oxygen to 1 part by weight of hydrogen.

QUESTIONS

1. Describe the laboratory preparation of hydrogen. What are its principal properties?

2. What weight of sulphuric acid would be required to prepare hydrogen in the laboratory, if 10 gm. of zinc are to be used up? What volume of hydrogen at S.T.P. would be obtained?

3. How is hydrogen prepared commercially?

4. Write an account of the uses of hydrogen.

5. How would you show that when hydrogen burns in air, water is formed?

6. How would you test a liquid to see if it contained water? What would you do to find out whether it was pure water or not?

7. What are the principal properties of water?

8. Describe an experiment by which you could determine the composition of water by volume.

9. Describe a method by which the composition of water by weight can be determined.

CHAPTER XIV

OXIDATION AND REDUCTION

Now that we have studied oxygen and hydrogen, we can get a clear idea of what is meant by the terms **oxidation** and **reduction.**

When a substance such as magnesium or hydrogen burns, it combines with oxygen from the air, forming an oxide. Such a reaction is called an oxidation.

When oxygen is removed from a compound, that is, the reverse of an oxidation, the reaction is called a reduction. That is, the gain of oxygen is an oxidation and the loss of oxygen is a reduction.

A substance that brings about an oxidation is called an *oxidizing agent.* Oxygen, then, is an oxidizing agent.

A substance that brings about a reduction is a *reducing agent.* Hydrogen is a reducing agent, because it can take oxygen away from certain compounds.

However, the terms oxidation and reduction have come to mean much more than is indicated above. Since hydrogen is instrumental in removing oxygen, i.e. in reducing, the addition of hydrogen to a substance is called a reduction, even though no oxygen may be concerned in the change at all.

We saw in the chapter on electrolysis that hydrogen and metals travel to the cathode, that is, the negative electrode. Hydrogen and metals are said to be *electropositive* elements. Oxygen and other non-metals and acid radicals travel to the anode, that is, the positive electrode, and these are said to be *electronegative* elements and radicals.

The term oxidation is now used to include, besides

oxygen, all electronegative elements or groups, and similarly reduction includes all electropositive elements. Thus:

Oxidation *is a chemical change during which there is a gain of oxygen or other electronegative element or group, or a loss of hydrogen or other electropositive element or group.*

Reduction *is a chemical change during which there is a gain of hydrogen or other electropositive element or group, or a loss of oxygen or other electronegative element or group.*

Some good oxidizing agents are:

Oxygen, nitric acid, ozone, chlorine, manganese dioxide, hydrogen peroxide.

Some examples of oxidation which we have already discussed are:

Magnesium and other elements burn in air to form oxides.

Iron is oxidized by steam to form iron oxide.

In the Bosch process for the manufacture of hydrogen, carbon is oxidized by steam to carbon monoxide, and the carbon monoxide oxidized by more steam (over a catalyst) to carbon dioxide.

Some good reducing agents are:

Hydrogen, nascent hydrogen, carbon, carbon monoxide, hydrogen sulphide, sulphur dioxide.

Hydrogen will reduce many metallic oxides to the metal, when passed over the heated oxide:

$$\text{e.g. } CuO + H_2 = H_2O + Cu.$$

Carbon will similarly reduce many metallic oxides. This is often done by heating strongly a mixture of the oxide and powdered charcoal:

$$2PbO + C = CO_2 + Pb.$$

We shall come across many other examples of oxidation and reduction in the course of our study of chemistry.

ACIDS, BASES, SALTS

Acids

We saw that non-metals give rise to acidic oxides, that is, oxides that dissolve in water to form acids. It is necessary to consider what we mean by an acid. The three commonest acids used in the laboratory are sulphuric acid, hydrochloric acid, and nitric acid, and there are others which we must study. Although these acids differ in their properties, they are all found to have common characteristics which group them together as substances of one class, namely, acids. These are the chief characteristics:

Acids generally have a sour taste.
Acids turn blue litmus red, and other " indicators " also give colour changes (p. 126).
Acids generally corrode metals.
Acids react with carbonates, giving off carbon dioxide gas.
Acids contain hydrogen, and when part or all of this hydrogen is replaced by a metal we get a substance known as a **salt.**

For example, if we replace the hydrogen in hydrochloric acid by sodium, we get sodium chloride:

$$HCl \rightarrow NaCl.$$

In sulphuric acid, however, there are two atoms of hydrogen in a molecule of the acid, and so we can replace either one or two:

$$H_2SO_4 \rightarrow NaHSO_4 \text{ or } Na_2SO_4.$$

The orthophosphoric acid molecule has three replaceable hydrogen atoms:

$$H_3PO_4 \rightarrow NaH_2PO_4 \text{ or } Na_2HPO_4 \text{ or } Na_3PO_4.$$

The number of replaceable hydrogen atoms in a molecule of an acid is called the *basicity* of the acid. Thus,

hydrochloric acid is *monobasic*, sulphuric acid is *dibasic*, and phosphoric acid is *tribasic*.

A salt derived from an acid where less than the full number of replaceable hydrogen atoms have been replaced by a metal is called an *acid salt*. Thus, $NaHSO_4$, sodium hydrogen sulphate, may be called acid sodium sulphate. It should be noted that an acid salt need not have an acid reaction.

Another characteristic of acids is that they react with bases to give salts and water only.

Historical note on acids

It will be remembered that in 1774 Lavoisier gave the name "oxygen" to Priestley's newly-discovered gas. The word "oxygen" is derived from two Greek words and signifies "acid-producer". Lavoisier found that certain substances formed oxides that dissolved in water to give acids, and came to the conclusion that "one of the most general properties of this element (oxygen) is to form acids by combining with many different substances". It was generally accepted then that oxygen was a necessary constituent of acids.

The discovery of two things, however, caused chemists (rather reluctantly) to abandon Lavoisier's oxygen theory of acids.

The first was due to Sir Humphry Davy, who showed that some oxides formed alkalis, and not acids, with water. As Davy rather caustically remarked, we may as well call Lavoisier's theory of acids his theory of alkalis.

The second was that certain acids do not contain oxygen; hydrochloric acid is one with which you are acquainted, and there are others.

The result of this new knowledge was that it was generally accepted that hydrogen, and not oxygen, is the essential element in an acid. It must be understood, as Davy was careful to point out, that although hydrogen is present in all acids and gives them their acid characteristics, all hydrogen compounds are not necessarily acids.

Bases

We saw (p. 101) that metals give rise to basic oxides. They are of two types: those which do not react with water, insoluble bases; and those which react with water to form hydroxides (soluble hydroxides being called alkalis). Some hydroxides, like ferric hydroxide, $Fe(OH)_3$, are insoluble. Both soluble and insoluble hydroxides are bases.

Bases, like acids, have common characteristics, the chief ones being as follows:

Soluble bases turn red litmus blue, and with other indicators also produce the opposite colour change to that produced by acids.

Bases generally liberate ammonia gas when heated with ammonium salts.

Bases react with acids, giving a salt and water only.

Salts

It is seen that bases are a sort of chemical opposite of acids, and that a salt is produced when these two opposites react. A salt is a *neutral* substance; it has characteristics neither of an acid nor of a base; it has no effect on litmus or other indicators. A base is said to *neutralize* an acid, and an acid to neutralize a base.

The relationship between metals, non-metals, acids, bases, and salts can be represented as follows:

$$
\begin{tikzcd}
& \text{Metal} \arrow[d] & \\
& \text{basic oxide} \arrow[dl] \arrow[dr, "\text{react with water}"] & \\
\textit{insoluble base} & & \textit{hydroxide}
\end{tikzcd}
$$

bases

$$
\begin{tikzcd}
\text{Non-metal} \arrow[d] \\
\text{acidic oxide} \arrow[d, "\text{react with water}"] \\
\textbf{acid}
\end{tikzcd}
$$

(*Note:* Some acids are not derived from oxides, and contain no oxygen.)

ACID + BASE → SALT + WATER.

Preparation of salts

(i) **From an acid and an insoluble base,** e.g.

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Add the insoluble base to the dilute acid, warming if the reaction is somewhat slow, until the solution is neutral to litmus and excess base is on the bottom of the beaker. (Do not dip the litmus paper in the solution; take out a drop of the liquid on the end of the stirring rod and touch the litmus paper with it.) Filter and evaporate the filtrate.

(ii) **From an acid and an alkali,** e.g.

$$NaOH + HCl = NaCl + H_2O.$$

Add the dilute acid, a little at a time and stirring the while, to a solution of the base until a drop of liquid extracted is found to be neutral to litmus. Filter if the liquid is not clear. Evaporate.

(iii) **From a metal and an acid,** e.g.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Add the metal to the dilute acid until effervescence ceases and excess metal is on the bottom of the beaker. The solution on testing is found to be neutral. Filter. Evaporate.

(iv) **From a carbonate and an acid.**

(*a*) *An insoluble carbonate*, e.g.

$$CuCO_3 + 2HNO_3 = Cu(NO_3)_2 + H_2O + CO_2.$$

Add the carbonate to the dilute acid until no more effervescence occurs and excess of the solid is at the bottom. The solution is now found to be neutral. Filter and evaporate.

(*b*) *A soluble carbonate*, e.g.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

Add the dilute acid, a little at a time, stirring, to a solution of the carbonate until a drop of liquid extracted proves to be neutral to litmus. Filter if the liquid is not clear. Evaporate.

(v) **From two salts (double decomposition).** This method is used to prepare insoluble salts, and this type of reaction, double decomposition, occurs frequently in qualitative analysis, e.g.

$$AgNO_3 + NaCl = \underset{\text{(insoluble)}}{AgCl} + NaNO_3.$$

A soluble silver salt and a soluble chloride are chosen to prepare insoluble silver chloride. The sodium nitrate formed is soluble, and so the silver chloride appears separately as a precipitate.

Indicators

Litmus has been mentioned above as an indicator. There are two others in common use, methyl orange and phenolphthalein. Their colours in acid, alkaline, and neutral solution are given in the table:

Indicator	In Acid Solution	In Alkaline Solution	In Neutral Solution
Litmus	red	blue	purple
Methyl orange	pink	yellow	orange
Phenolphthalein	colourless	red	colourless

QUESTIONS

1. What is meant by the terms *oxidation, reduction, oxidizing agent, reducing agent*?

2. Name three good oxidizing agents, and give an example of an oxidation carried out with each.

3. Describe two methods by which you could reduce lead oxide in the laboratory.

4. What is meant by the terms *acid, base, alkali, salt*?

5. State the principal properties of acids, and take sulphuric acid as an example to illustrate these properties.

6. Explain the term *basicity* of an acid. What is meant by an *acid salt*?

7. Outline Lavoisier's oxygen theory of acids, and indicate how it was overthrown.

8. How would you prepare crystals of magnesium sulphate, given a short length of magnesium ribbon?

9. Describe two ways by which you could prepare crystals of copper sulphate

10. How may crystals of sodium sulphate be prepared in the laboratory?

11. Barium sulphate is insoluble in water. How would you prepare a specimen of barium sulphate in the laboratory?

12. What weight of silver nitrate is necessary to precipitate 3 gm. of silver chloride, by adding silver nitrate solution to a solution of common salt?

CHAPTER XV

NITROGEN: AMMONIA

NITROGEN

Occurrence

Nitrogen occurs in the free state to the extent of about four-fifths of the atmosphere by volume. In combination it occurs in many salts, particularly as nitrates and ammonium salts.

It is present in all animal and vegetable organisms.

Preparation

Nitrogen may be prepared from the atmosphere by removing the other constituents.

An aspirator is allowed to fill slowly with water, so that a slow stream of air passes through a bottle containing sodium hydroxide solution, which removes the

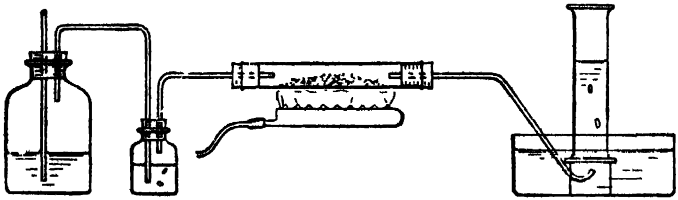


Fig. 27. — Preparation of Atmospheric Nitrogen

carbon dioxide, and over heated copper filings, which remove the oxygen (fig. 27).

The sodium hydroxide solution readily absorbs the carbon dioxide:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

The absorption of the oxygen by the heated copper is slow, and so the air must be passed over very slowly:

$$2Cu + O_2 = 2CuO.$$

As we have removed carbon dioxide and oxygen, the gas collecting in the gas jar is nitrogen, if we assume that these three gases are the only constituents of the atmosphere. (If dry nitrogen were required, the water vapour in the air could, of course, be removed by passing over calcium chloride, and then the gas would have to be collected over mercury.)

Until comparatively recently it was thought that these were the only gases in the atmosphere, and that this residual gas was pure nitrogen. **Sir William Ramsay**, on finding that the density of atmospheric nitrogen was greater than that of chemically prepared nitrogen, assumed that the nitrogen from the air contained another inert and heavier gas. To isolate this gas he removed carbon dioxide, water vapour, and oxygen from the air, and then removed the nitrogen from the residual gas by passing it over heated magnesium The magnesium combines with nitrogen, forming magnesium nitride:

$$3Mg + N_2 = Mg_3N_2.$$

He found that a small quantity of gas was left, and to it he gave the name **argon**. Later, this gas was liquefied, and on evaporation was found to consist of a mixture of several gases. Argon, neon, and helium are the most important of the inert gases, other than nitrogen, contained in the atmosphere.

Argon is used to fill electric filament lamps. Neon is used for non-filament lamps for red electric signs. Helium, which occurs in the " natural gas " of American oil regions, is used in America for filling airships.

Nitrogen free from other inert atmospheric gases may be prepared by heating a solution of ammonium nitrite.

Ammonium nitrite is, however, unstable, and so it is prepared as required by heating ammonium chloride and sodium nitrite. The resulting ammonium nitrite is decomposed as soon as it is formed:

$$NH_4Cl + NaNO_2 \rightleftharpoons NH_4NO_2 + NaCl.$$
$$NH_4NO_2 = N_2 + 2H_2O.$$

Notice that the first equation indicates a reversible reaction. The fact that the ammonium nitrite decom-

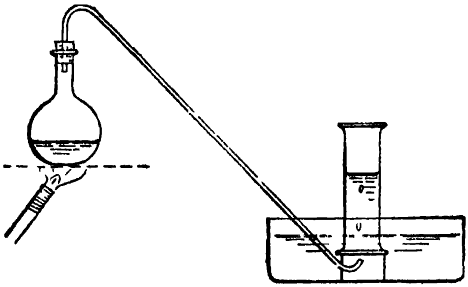


Fig. 28. — Preparation of Nitrogen from Ammonium Nitrite

poses and nitrogen goes away as a gas, causes the reaction to proceed from left to right.

Equimolecular proportions of ammonium chloride and sodium nitrite are dissolved in water and heated in a round-bottomed flask. The nitrogen is collected over water (fig. 28).

Nitrogen can also be prepared by heating crystals of ammonium dichromate:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

Ammonia can be oxidized to nitrogen by chlorine or by copper oxide. In the case of chlorine, this gas is passed into a strong solution of ammonia:

$$2NH_3 + 3Cl_2 = 6HCl + N_2.$$

(The HCl formed immediately combines with ammonia, giving ammonium chloride:

$$HCl + NH_3 = NH_4Cl.)$$

In this experiment the ammonia must be present in excess, otherwise there is a risk of a dangerously explosive compound of nitrogen and chlorine being formed.

In the oxidation of ammonia by copper oxide, the ammonia gas is passed over the heated copper oxide:

$$2NH_3 + 3CuO = 3Cu + 3H_2O + N_2.$$

Properties

Nitrogen is a colourless, odourless gas with a density a little less than that of air. It is very slightly soluble in water. It does not burn or support combustion.

It is recognized in the laboratory by its negative rather than by its positive properties. If we find that we have a colourless, odourless gas which does not burn or support combustion, it is almost certainly either nitrogen or carbon dioxide. If the gas is bubbled through lime water and no turbidity is observed, the gas is not carbon dioxide, and so we assume that it is nitrogen.

Nitrogen has positive properties, however, and two of these in particular are of great importance: it combines, under suitable conditions, with oxygen to form nitric oxide, and with hydrogen to form ammonia. The importance of these properties is that they enable nitric acid and ammonia to be manufactured, the nitrogen coming from the atmosphere. (See pp. 142 and 137.)

Nitrogen combines with some metals on heating, forming nitrides, e.g.

$$3Mg + N_2 = Mg_3N_2.$$

When magnesium burns in air, the white ash formed is mostly magnesium oxide, but some magnesium nitride is also present.

AMMONIA

Occurrence

Ammonia occurs to a very small extent in the atmosphere. Ammonium salts occur in the earth's crust.

Preparation

Ammonia is evolved when any ammonium salt is heated with any alkali. It is usual to heat ammonium chloride with calcium hydroxide (slaked lime). The gas

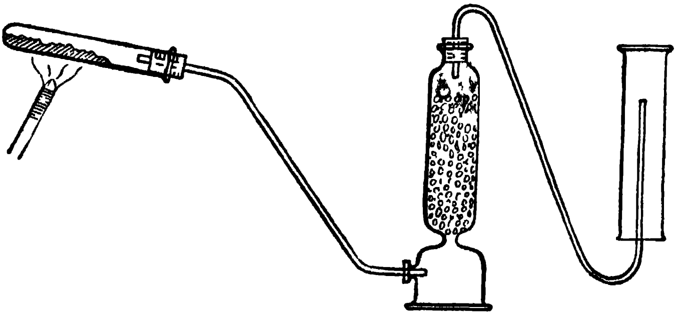


Fig. 29. — Preparation of Ammonia

is dried in a drying tower containing calcium oxide (quicklime), as it reacts with the usual drying agents, calcium chloride and sulphuric acid. It is lighter than air, and so is collected by downward displacement of air (fig. 29).

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2H_2O + 2NH_3.$$

If a greater quantity of gas is required, the mixture may be heated in a round-bottomed flask instead of the hard glass test-tube, but it should slope downwards towards the neck, or condensed steam will run back on to the hot dry mixture and crack the flask.

Properties

Ammonia is a colourless gas with a distinctive pungent smell. It is lighter than air and is extremely soluble in water. The gas may easily be liquefied by compressing it.

The extreme solubility of ammonia in water may be demonstrated by what is known as the *fountain experiment.*

A round-bottomed flask is substituted for one of the gas jars when collecting ammonia, and when full of the gas it is closed by a bung fitted with glass tubing as shown. The flask is clamped vertically with the tube under water in a large beaker (fig. 30). The ammonia begins to diffuse into the tube, and after some minutes water will rise up the tube slowly as ammonia reaches the water-level and dissolves. As soon as the water reaches the top, however, it will rush out of the jet in a fountain and finally nearly fill the flask. The remaining small space will be due to the ammonia having contained a little air.

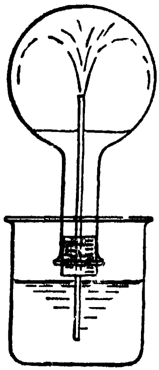


Fig 30.—Solubility of Ammonia — the Fountain Experiment.

If the water in the beaker is first made slightly acid and litmus solution added, the red colour will be changed to blue as the liquid rushes into the flask, showing that the solution is an alkali. It contains the base ammonium hydroxide:

$$NH_3 + H_2O = NH_4OH.$$

This base gives rise to a series of salts called ammonium salts, where the ammonium radical, NH_4, behaves like the metal in other salts. For example, compare

$$NaOH + HCl = NaCl + H_2O$$

with

$$NH_4OH + HCl = NH_4Cl + H_2O.$$

Note that ammonia itself is not a true base, because with an acid it forms a salt but no water:

$$NH_3 + HCl = NH_4Cl.$$

Ammonia, NH_3, is called a *basic anhydride*; with water it forms a true base, ammonium hydroxide.

The reaction of ammonia with hydrogen chloride is interesting. A gas jar full of ammonia is inverted over a similar jar full of hydrogen chloride, each being covered (fig. 31). On removing the covers and allowing the gases to come into contact, dense white fumes of ammonium chloride are formed, which settle on the sides of the gas jar as a white powder:

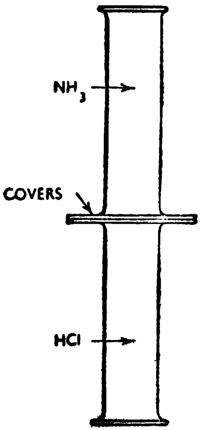


Fig. 31. — Action of Ammonia and Hydrogen Chloride.

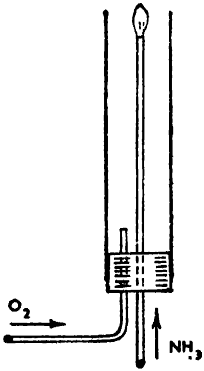


Fig. 32. — Ammonia burning in Oxygen.

$$NH_3 + HCl = NH_4Cl.$$

Although ammonia does not burn in air, it does so in an atmosphere of oxygen. The apparatus shown in fig. 32 is fitted up so that when the ammonia emerges

from the jet it is surrounded by oxygen. The gas issuing from the jet can be lit and will continue to burn:

$$4NH_3 + 3O_2 = 6H_2O + 2N_2.$$

As has been said, ammonia can be oxidized by chlorine to nitrogen. The chlorine is, as can be seen from the equation, reduced to hydrogen chloride.

It was also seen that copper oxide oxidizes ammonia to nitrogen. At the same time, of course, the copper oxide is reduced.

Hence, ammonia is a reducing agent.

Tests for ammonia

Ammonia gas can, of course, easily be recognized when evolved, by its most distinctive smell. Also, it turns moist red litmus paper blue, and white fumes of ammonium chloride are formed when a stirring rod with a drop of concentrated hydrochloric acid on the end is held in the gas.

Ammonia in solution, and ammonium salts, can be detected in very minute quantities by what is known as *Nessler's solution*. Ammonia gives a brown precipitate or a brownish-yellow coloration with it. To make Nessler's solution, add potassium iodide solution to mercuric chloride solution until the precipitate of mercuric iodide formed just redissolves:

$$2KI + HgCl_2 = 2KCl + \underset{\text{(mercuric iodide, ppt.)}}{HgI_2}.$$

$$HgI_2 + 2KI = \underset{\text{(potassium mercuri-iodide. Soluble.)}}{K_2HgI_4}.$$

This solution is then made alkaline with sodium hydroxide solution.

Composition of ammonia

A long tube, marked off into three equal parts, is filled with chlorine (fig. 33). It is closed by a stopper fitted with a dropping funnel containing strong ammonia solution. A drop of the solution is allowed to fall into the tube, when a violent action occurs, accompanied by a flash and white fumes:

$$2NH_3 + 3Cl_2 = 6HCl + N_2.$$

(The white fumes are due to solid ammonium chloride formed from the hydrogen chloride produced and some of the ammonia.)

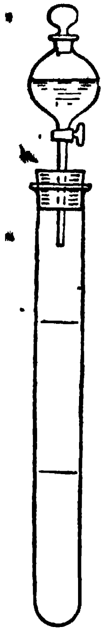


Fig. 33. — Volumetric Composition of Ammonia. Hoffman's Method.

More ammonia solution is admitted drop by drop until there is no further reaction. Then the solution in the funnel is replaced by water. On admitting this water (the funnel must be kept filled up with water—one filling will not be enough) the hydrogen chloride dissolves, leaving the nitrogen. This is found to fill one-third of the tube.

In this reaction the chlorine has combined with the hydrogen of the ammonia, and it is known that chlorine and hydrogen combine in equal volumes. We started with three volumes of chlorine, and therefore three volumes of hydrogen in the ammonia were used. It was observed that one volume of nitrogen was left.

Hence, ammonia consists of three volumes of hydrogen combined with one volume of nitrogen, and so, from Avogadro's principle:

Three *molecules* of hydrogen combine with one *molecule* of nitrogen, to form ammonia.

That is, six *atoms* of hydrogen combine with two *atoms* of nitrogen, to form ammonia.

Therefore, the *simplest* formula is NH_3. From this experiment the formula could be any multiple of NH_3.

Density determinations, however, show that the gas has a density of 8·5 (H = 1).

Therefore the molecular weight = 2 × 8·5 = 17.

But the atomic weights of nitrogen and hydrogen are 14 and 1 respectively.

Hence the formula of ammonia is NH_3.

Industrial preparation

The Haber process.—Nitrogen and hydrogen are found to combine in the presence of a suitable catalyst:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

In the above reversible reaction it is found that as the temperature rises, the speed of the forward reaction increases, but that of the reverse reaction increases faster, so that the equilibrium percentage of ammonia formed decreases with rise of temperature. However, at low temperatures, the reaction is so slow as to be useless, so a compromise has to be reached. Matters are helped by the fact that increase in pressure increases the equilibrium percentage of ammonia. The synthesis is performed at 550° C. and a pressure of 200 atmospheres. Some processes work at much higher pressures even than this.

The catalyst generally used is a specially purified iron with molybdenum added. The gases are introduced in correct proportions, compressed, and sent over the heated catalyst. The ammonia formed is cooled, and at that pressure it liquefies and is taken off. The uncombined gases are pumped back to the catalyst together with more nitrogen and hydrogen (fig. 34).

The hydrogen is prepared by the Bosch process (p. 111),

and the nitrogen from producer gas (p. 219) removing the carbon monoxide by oxidizing it with steam and removing the resulting carbon dioxide by washing with water under pressure.

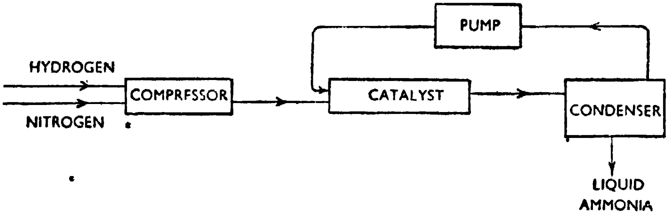


Fig. 34. — Diagram of Synthesis of Ammonia

From gas liquor. — When coal is distilled, one of the products is ammonia. This is absorbed in water, distilled out, and converted by sulphuric acid into ammonium sulphate.

Uses of ammonia

Ammonia is used for ice machines and refrigerators. The gas is compressed and made to liquefy in coils

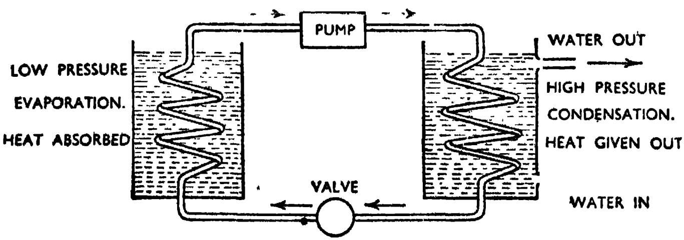


Fig. 35. — Principle of the Refrigerator

(fig. 35). Cold water circulates around these coils to absorb the heat given out. The liquid ammonia is forced through a regulating valve to the low-pressure part of the machine, where it evaporates and in doing so takes in

heat. The gas is then recompressed and the cycle repeated.

Ammonia is used for softening water in laundries. The calcium bicarbonate in the water causing the hardness (p. 249) is changed into the insoluble carbonate:

$$Ca(HCO_3)_2 + 2NH_4OH = CaCO_3 + (NH_4)_2CO_3 + 2H_2O.$$

The ammonium hydroxide also helps to clean the articles, as it neutralizes acids and dissolves grease.

Ammonia is also used in the manufacture of nitric acid.

Ammonium salts

Ammonium salts may readily be recognized because they give off ammonia gas when heated with an alkali, e.g. sodium hydroxide. The gas is recognized by its distinctive smell and by its action on red litmus paper.

Ammonium sulphate, $(NH_4)_2SO_4$, is a white crystalline solid soluble in water. It is produced in gas works, or from the ammonia made by the Haber process. It is used as a fertilizer and to make ammonium chloride.

Ammonium chloride, NH_4Cl, is known as *sal ammoniac*. It is a white crystalline soluble solid which sublimes on heating, the vapour splitting up into ammonia and hydrogen chloride:

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

On cooling, the ammonia and hydrogen chloride recombine to form the solid ammonium chloride.

A reversible decomposition such as this is called *dissociation.*

Ammonium chloride is used as the electrolyte in wet and dry Leclanché cells, and as a flux in soldering. The heat of the soldering iron causes some ammonium chloride to dissociate, and the hydrogen chloride cleans the metal, enabling the solder to stick to it.

Ammonium nitrate is a white crystalline soluble

solid, and is made from ammonia and nitric acid. It is used in the preparation of nitrous oxide, the nitrate decomposing on heating:

$$NH_4NO_3 = N_2O + 2H_2O.$$

It is also used as a constituent of explosives. Amatol, used as a high explosive, is a mixture of it and trinitrotoluene (T.N.T.).

QUESTIONS

1. How would you prepare in the laboratory nitrogen from the air as pure as possible? In what ways would the gas you obtained differ from chemically pure nitrogen?

2. Describe the preparation of pure nitrogen.

3. What are the properties of nitrogen? Why is atmospheric nitrogen of great importance industrially?

4. How would you prepare ammonia in the laboratory?

5. What are the principal properties of ammonia? How would you demonstrate that it is very soluble in water?

6. Give reasons for saying that ammonia is a reducing agent.

7. Describe a method for determining the volumetric composition of ammonia. For what reasons may it be assumed that the formula for ammonia is NH_3?

8. Describe the Haber process for the industrial preparation of ammonia. What are the principal uses of ammonia?

9. What are the chief properties and uses of ammonium sulphate, ammonium chloride, and ammonium nitrate?

10. What weight of ammonium chloride is necessary to prepare two litres of ammonia at S.T.P.?

CHAPTER XVI

NITRIC ACID

Occurrence

Nitric acid, HNO_3, has been known from very early times. It was called "aqua fortis" — strong water. It occurs in the free state in the atmosphere to a small degree. Nitrates occur abundantly in the soil, particularly in Chile, where the sodium nitrate deposits (Chile saltpetre) cover an area of over 300 square miles.

Laboratory preparation

Nitric acid is formed by the action of concentrated sulphuric acid on any nitrate, and is usually prepared in the laboratory from potassium nitrate. It is one of the few occasions on which that symbol of chemistry, a retort, is used in a school laboratory. This is because in that apparatus there are no rubber or cork parts, which would be attacked by the acid.

Crystals of potassium nitrate are placed in the retort. Concentrated sulphuric acid is added and the retort heated gently. Soon brown fumes are observed, and nitric acid condenses in the receiving flask, which is kept cool by a stream of water over it (fig. 36):

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

Notice that only one of the two atoms of the sulphuric acid molecule has been replaced by a potassium atom; on heating strongly, the other hydrogen atom would be replaced, but the higher temperature would result in

decomposition of a considerable quantity of the nitric acid.

The acid obtained is seen to be of a yellow colour. This is due to the decomposition of some of the nitric

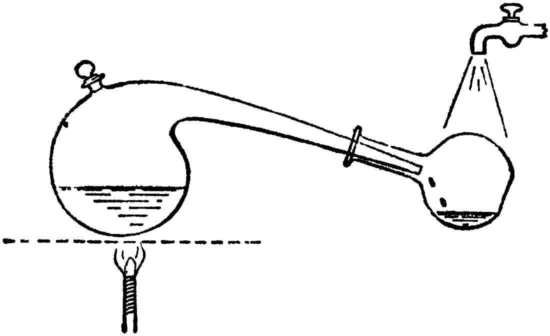


Fig 36. — Preparation of Nitric Acid

acid, forming nitrogen peroxide, which dissolves in the rest of the acid, colouring it.

Industrial preparation.

(1) **From sodium nitrate** (from the Chilean deposits). — The manufacture is as described in the laboratory preparation above, using iron retorts and earthenware receivers.

(2) **Birkeland and Eyde's process.** —This is one of the methods for the fixation of atmospheric nitrogen. Nitrogen and oxygen, both present in the air, are passed through an electric arc which is drawn out into a large flaming disc by means of electromagnets. Under these conditions small proportions of the gases combine to form nitric oxide:

$$N_2 + O_2 = 2NO.$$

On cooling, the nitric oxide is oxidized by oxygen from the air to form nitrogen peroxide:

$$2NO + O_2 = 2NO_2.$$

The nitrogen peroxide and air are washed with water, when nitric acid is formed:

$$4NO_2 + O_2 + 2H_2O = 4HNO_3.$$

In this process the nitric acid is generally converted by excess of lime into basic calcium nitrate, which is sold as a fertilizer under the name of *Norwegian saltpetre.*

(3) **By the oxidation of synthetic ammonia.** — This is the most modern and most efficient process for the large-scale production of nitric acid.

The ammonia is prepared by the Haber process as described on p. 137. The ammonia is then oxidized by air, by passing the mixture over platinum as a catalyst at a temperature of 500° C. This forms nitric oxide:

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

The nitric oxide is oxidized and absorbed by water to form nitric acid as in the Birkeland-Eyde process.

Properties

Nitric acid is a colourless fuming liquid, boiling at 85° C., and having a specific gravity of 1·5. It is very corrosive and attacks the skin and clothes, so care has to be taken in its use.

It exhibits the properties of acids; for example, it neutralizes bases to form salts (**nitrates**):

$$HNO_3 + NaOH = NaNO_3 + H_2O.$$

One important property is that it is a powerful oxidizing agent. For example, when it reacts with metals, the hydrogen first produced is immediately oxidized, by more acid, to water, and the acid is decomposed. Thus, with copper and somewhat diluted nitric acid, nitric oxide is formed:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO,$$

and with lead, nitrogen peroxide is liberated:

$$Pb + 4HNO_3 = Pb(NO_3)_2 + 2H_2O + 2NO_2.$$

Another example of the oxidizing action of nitric acid is shown in its reaction with sulphur, which it oxidizes to sulphuric acid:

$$S + 6HNO_3 = 2H_2O + 6NO_2 + H_2SO_4,$$

Notice that the oxidizing agent itself undergoes reduction. That is, the nitric acid is reduced to nitrogen peroxide.

In a similar way, carbon is oxidized to carbon dioxide, and phosphorus to phosphoric acid, the nitric acid in each case being reduced to nitrogen peroxide.

Ferrous sulphate is oxidized to ferric sulphate, the nitric acid being reduced this time to nitric oxide. This nitric oxide combines with excess of ferrous sulphate to form the compound $(FeSO_4)_2NO$, a brown substance. This reaction is used in the *brown ring test* for nitric acid and nitrates.

Brown ring test for nitric acid and nitrates

To a small portion of the nitrate solution add some cold concentrated ferrous sulphate solution. (This is made by shaking up crystals of ferrous sulphate with water to which a drop or two of dilute sulphuric acid has been added.) Now pour some concentrated sulphuric acid carefully down the side of the test-tube. It will sink to the bottom, forming a layer under the other lighter liquid. Where the two liquids meet, a brown ring will be formed.

The concentrated sulphuric acid first reacts with the nitrate to give nitric acid. This is reduced by some of the ferrous sulphate to nitric oxide. The nitric oxide attaches itself to more ferrous sulphate to form the brown compound $(FeSO_4)_2NO$.

OXIDES OF NITROGEN

Nitrogen forms five oxides. They are:

Nitrous oxide, N_2O.
Nitric oxide, NO.
Nitrogen trioxide, N_2O_3.
Nitrogen peroxide, NO_2.
Nitrogen pentoxide, N_2O_5.

The composition of these oxides provides an excellent illustration of the Law of Multiple Proportions. It is found that the weights of oxygen which separately combine with a fixed weight of nitrogen are in the simple ratio of 1 : 2 : 3 : 4 : 5.

Nitrous oxide, N_2O

This gas is generally prepared by heating ammonium nitrate:

$$NH_4NO_3 = N_2O + 2H_2O.$$

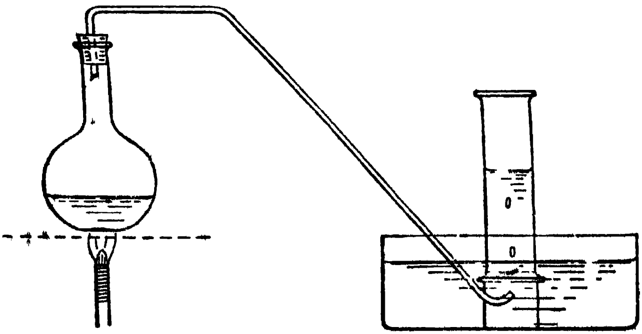


Fig. 37. — Preparation of Nitrous Oxide

Crystals of ammonium nitrate are placed in a flask and heated gently (fig. 37). The nitrate is seen to melt, and then decomposes, nitrous oxide being evolved. (Do

not heat for a time sufficient to decompose all the ammonium nitrate, as it is liable to explode if reduced in bulk too much.)

The gas is collected over hot water, as it is appreciably soluble in cold water. Nitrous oxide thus prepared generally contains a little nitric oxide as impurity. This can be removed by bubbling it through ferrous sulphate solution.

Properties. — Nitrous oxide is a colourless gas with a faint sweet smell. It is fairly soluble in water.

It supports combustion more vigorously than air, but less so than oxygen. It does so sufficiently to rekindle a glowing splint of wood.

The gas may be easily distinguished from oxygen by means of its faint smell, its solubility in water, and the fact that it does not give brown fumes with nitric oxide.

Use. — The chief use of nitrous oxide is as an anæsthetic for minor operations, notably in dentistry. Hysteria sometimes follows recovery from the anæsthetic, and this gave rise to the name " laughing gas ".

Nitric oxide, NO

Nitric oxide is prepared by the action of 50 per cent nitric acid on copper:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Equal volumes of concentrated nitric acid and water are mixed, and the mixture added through a thistle funnel to copper turnings in a flask or Woulfe bottle. No heating is necessary. The gas is collected over water.

Properties. — Nitric oxide is a colourless gas which will not burn but will support combustion of strongly burning substances. Phosphorus which is burning slowly will be extinguished when plunged into a jar of nitric oxide; but if burning vigorously, it will continue to do so in the gas. In the second case the heat of the flame is sufficient to decompose the nitric oxide into nitrogen and oxygen; in the first case it is not.

Nitric oxide has the distinctive property of forming brown fumes in air or oxygen. This is due to its oxidation to nitrogen peroxide:

$$2NO + O_2 = 2NO_2.$$

As this is so, it is quite impossible to say whether nitric oxide has a smell or not; because as soon as the gas is exposed, nitrogen peroxide is formed, and it is this gas that is smelt.

The action of nitric oxide with ferrous sulphate has already been described. The compound $(FeSO_4)_2NO$ formed decomposes on heating, giving off nitric oxide. This fact is utilized when it is necessary to prepare pure nitric oxide, which is done as follows: nitric acid is added to copper turnings as before, and the somewhat impure nitric oxide evolved is passed into a solution of ferrous sulphate. The dark brown solution formed is placed in another flask and heated, and the pure nitric oxide collected.

Nitrogen peroxide, NO_2

This is generally prepared in the laboratory by heating lead nitrate:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

As a mixture of nitrogen peroxide and oxygen is evolved, the two gases must be separated. This is done by passing them into a U-tube surrounded by a freezing mixture (fig. 38, p. 148). The nitrogen peroxide liquefies and the oxygen passes on.

(Nitrates of other heavy metals give off nitrogen peroxide and oxygen on heating, but are unsuitable as they contain water of crystallization. This would be evolved and would condense and freeze in the U-tube.)

The liquid nitrogen peroxide obtained is a greenish-yellow liquid, but when pure it is yellow.

Properties. — Nitrogen peroxide is a red-brown gas with a strong pungent smell. Great care should be

taken in observing the smell: take a breath of air and then sniff a little of the gas carefully, breathing out strongly immediately afterwards; the gas is dangerous if inhaled.

It readily condenses to a yellow liquid which boils at 22° C.

Density determinations show that the gas has the formula N_2O_4 at temperatures just above the boiling-point, the vapour density being 46 and the molecular weight therefore 92. ($N_2 = 2 \times 14$, $O_4 = 4 \times 16$.)

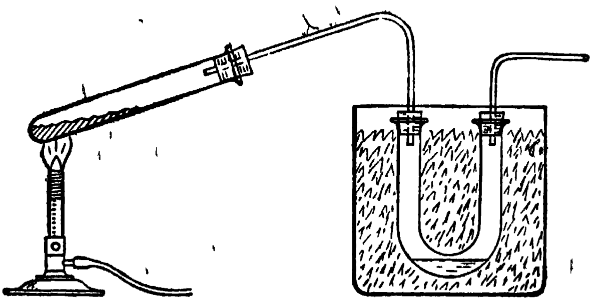


Fig. 38. — Preparation of Nitrogen Peroxide

On heating, however, the vapour density is found gradually to diminish, until at 150° C. and above it is 23. That is, the molecular weight is 46, which corresponds with the formula NO_2. ($N = 14$, $O_2 = 2 \times 16$.) This is another case of dissociation:

$$N_2O_4 \rightleftharpoons 2NO_2.$$

At 22° C. it is N_2O_4, at and above 150° C. it is NO_2, and between these two temperatures it is a mixture of the two.

Nitrogen peroxide, like nitrous oxide and nitric oxide, supports combustion of strongly burning substances. The gas is decomposed and it is the oxygen that supports the combustion.

On shaking the gas up with water, a mixture of nitric and nitrous acids is formed:

$$2NO_2 + H_2O = \underset{\text{(nitric acid)}}{HNO_3} + \underset{\text{(nitrous acid)}}{HNO_2}.$$

An important property of nitrogen peroxide is that it oxidizes sulphur dioxide, in the presence of water vapour, to sulphuric acid:

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO.$$

This reaction is important in the manufacture of sulphuric acid by the lead chamber process (see p. 189).

THE NITROGEN CYCLE

All plants need nitrogen in order to grow, the protein in plants (and animals) being a complex nitrogen compound. This nitrogen is obtained from nitrates in the soil. Most plants cannot absorb nitrogen direct from the air, and so nitrogen compounds in the soil are essential for growth. Plants decay, and some of the nitrogen goes back into the soil; ammonium salts produced in the decomposition of the plant are changed by bacterial action into nitrites and finally into nitrates, ready to be absorbed again by other plants. Other nitrogen from decaying plants goes into the atmosphere as ammonia. Some plants are eaten by animals, and the nitrogen goes to form the protein in the animals. Other animals eat animals to get their protein. The excretions of the animal return the nitrogen compounds to the soil, and when the animal dies, the decay of his body does likewise.

Certain plants, called leguminous plants, can absorb free nitrogen from the air, and turn it, by the aid of bacteria on their roots, into nitrogen compounds, part of which are used by the plant itself, the surplus remaining to enrich the soil.

Lightning and other electric discharges in the air cause

some of the atmospheric nitrogen and oxygen to combine, forming nitric oxide and finally nitric acid, which the rain washes into the soil. Some of the nitrogen lost into the air as ammonia is neutralized by this nitric acid and the resulting ammonium nitrate goes into the soil.

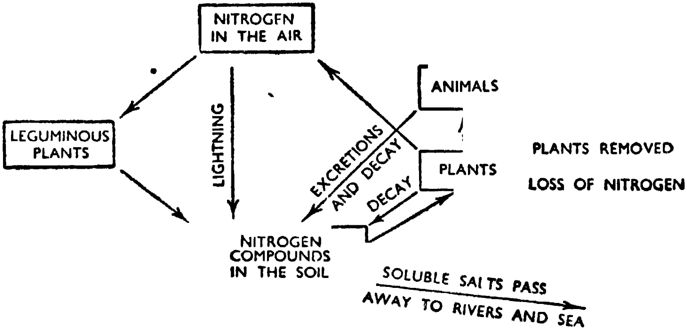


Fig. 39. — The Nitrogen Cycle

Under natural conditions this nitrogen cycle (fig. 39) maintains a balance and the soil remains fertile. Under modern conditions, however, when acres of plants are removed (e.g. from wheat fields) to feed people in towns, the loss of nitrogen from the soil is serious. This loss is made up by the addition of artificial fertilizers in the form of nitrates and ammonium salts, much of which is now prepared from the atmosphere, where the supply of nitrogen is limitless.

QUESTIONS

1. How is nitric acid prepared in the laboratory? Why is the sample so obtained somewhat yellow in colour?

2. Describe the Birkeland-Eyde process and the ammonia process for the industrial preparation of nitric acid. Why are these two processes of vital importance to modern civilization?

3. Give reasons for saying that nitric acid is an oxidizing agent.

4. How is nitrous oxide prepared? What are its principal properties?

5. Write an account of the preparation and properties of nitric oxide.

6. How would you prepare nitrogen peroxide in the laboratory? What are its chief properties?

7. Write an essay on "The Nitrogen Cycle in Nature".

CHAPTER XVII

CHLORINE: HYDROCHLORIC ACID

Occurrence

Chlorine does not occur in nature in the free state, but it occurs widely in combination, chiefly as chlorides, the most common being sodium chloride, common salt. This occurs in sea water, in the earth as rock salt, and in salt springs.

Chlorine was first prepared by the Swedish chemist **Scheele** in 1774, by the action of hydrochloric acid (then called " muriatic acid ") on manganese dioxide. He considered it as being muriatic acid deprived of its phlogiston by the manganese. A little later, the French chemist **Berthollet** found that a solution of chlorine in water gave off bubbles of oxygen, and, being a supporter of Lavoisier's theory, he called the gas " oxymuriatic acid " — considering it to be a compound of muriatic acid and oxygen.

Davy, however, in 1810, failed to obtain any oxygen compound by heating numerous elements in the gas, and so said it should be considered to be an element. He called it chlorine, from its colour. Berthollet's observation he explained by saying that the oxygen evolved must have come from the water.

Laboratory preparation

The usual laboratory preparation is by the oxidation of hydrochloric acid, the oxidizing agent being manganese dioxide:

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2.$$

The manganese dioxide is placed in a round-bottomed flask fitted with a thistle funnel and delivery tubing leading to a gas jar (fig. 40). The delivery tubing goes through a piece of cardboard which acts as a cover to the gas jar while the gas is being collected.

Concentrated hydrochloric acid is poured down the thistle funnel, and the flask is gently heated. The chlorine

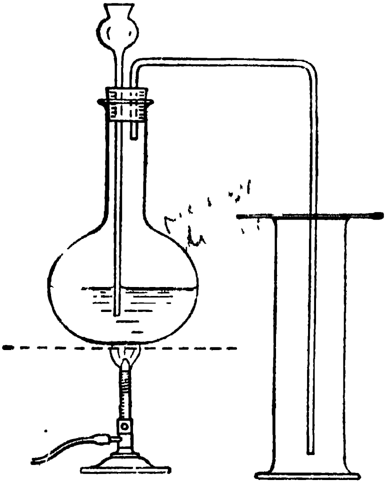


Fig. 40. — Preparation of Chlorine

is seen to be evolved and will collect in the gas jar. When the green colour of the gas reaches the top of the jar, another jar is quickly put in its place, the full jar being immediately closed by a glass cover. When sufficient gas has been collected, the apparatus is placed in the fume cupboard, if the experiment was not conducted therein.

The manganese dioxide acts as an oxidizing agent because each molecule contains one atom of oxygen above the normal amount necessary to satisfy the manganese atom. The valency of manganese is 2, and so is that of oxygen. The normal oxide, therefore, is MnO. That is,

the oxidation of the hydrochloric acid and the simultaneous reduction of the manganese dioxide will be according to the equation:

$$MnO_2 + 2HCl = MnO + H_2O + Cl_2.$$

The MnO formed, however, being a basic oxide, will react with the hydrochloric acid present, forming a salt and water, thus:

$$MnO + 2HCl = \underset{\text{(manganous chloride)}}{MnCl_2} + H_2O.$$

The equation given just before the diagram is a combination of these two equations, and represents the total reaction.

The gas obtained by this method contains some hydrogen chloride as an impurity. If necessary this can be removed by bubbling the gas through a small quantity of water. If the gas is needed dry, it is bubbled through concentrated sulphuric acid.

Other oxidizing agents will oxidize hydrochloric acid to chlorine, and one, potassium permanganate, provides a convenient method sometimes used in the laboratory. Potassium permanganate, like manganese dioxide, has more than its share of oxygen, and it readily parts with it. Five atoms of oxygen are available from every two molecules of potassium permanganate. The equation is rather difficult, but the actual oxidation may be represented by

$$\underset{\text{(from }2KMnO_4)}{5O} + 10HCl = 5H_2O + 5Cl_2.$$

In this method the concentrated hydrochloric acid is added from a dropping funnel to potassium permanganate contained in a flask. The evolution of gas is immediate, without heating, and so the stream of chlorine may be controlled, and stopped when sufficient has been obtained.

Industrial preparation

Chlorine used to be obtained commercially by the oxidation of hydrochloric acid. In one process the oxidizing agent was manganese dioxide, and in another, air, using cuprous chloride as a catalyst.

Nowadays it is mostly obtained as a by-product in the preparation of sodium hydroxide by the electrolysis of brine (see p. 233). The chlorine is liquefied by pressure and stored in iron cylinders.

Properties

Chlorine is a yellowish-green gas with a pungent smell. It is about 2½ times as dense as air, and dissolves in water. It is a poison and was used in warfare as a poison gas until superseded by "better" gases. The gas readily liquefies on compressing.

Bleaching action of chlorine. — Moist chlorine bleaches most dyes, including writing ink. The gas turns moist blue litmus paper red and then white. The bleaching is due to oxidation of the coloured substances, and only occurs in the presence of water.

If a solution of chlorine in water, *chlorine water*, is placed in sunlight, oxygen is evolved and hydrochloric acid is found to be in the solution. The chlorine reacts with the water, giving hypochlorous acid and hydrochloric acid:

$$Cl_2 + H_2O = HCl + \underset{\text{(hypochlorous acid)}}{HClO}.$$

The hypochlorous acid is unstable, and decomposes:

$$HClO = HCl + O.$$

The oxygen atoms combine in pairs, of course, and molecules of oxygen are evolved. But if the oxygen atoms are liberated in close proximity to molecules of the coloured dye, this nascent oxygen is sufficiently active

to oxidize them. The oxidation products are white, and so bleaching occurs.

Dry chlorine will not bleach. This may be shown as follows:

Into a gas jar containing chlorine place some dry coloured material, and into another some of the same material moistened with water. The moist cloth will quickly bleach; the dry will remain unchanged.

Formation of chlorides

Chlorine combines directly with metals and some non-metals to form **chlorides.**

Phosphorus burns spontaneously when plunged into a jar of chlorine, giving a mixture of phosphorus tri-chloride and pentachloride:

$$3Cl_2 + 2P = \underset{\text{(phosphorus trichloride)}}{2PCl_3}.$$

$$5Cl_2 + 2P = \underset{\text{(phosphorus pentachloride)}}{2PCl_5}.$$

Dutch metal (a thin metal foil, consisting of 80 per cent copper and 20 per cent zinc, and used as a substitute for gold leaf in electroscopes) also catches fire spontaneously when plunged into chlorine. Copper chloride and zinc chloride are formed:

$$Cu + Cl_2 = \underset{\text{(copper chloride)}}{CuCl_2}.$$

$$Zn + Cl_2 = \underset{\text{(zinc chloride)}}{ZnCl_2}.$$

Burning sodium in a deflagrating spoon continues to burn when plunged into a gas jar of chlorine, forming sodium chloride:

$$2Na + Cl_2 = 2NaCl.$$

If chlorine is passed over heated iron wire, black crystals of ferric chloride are formed:

$$2Fe + 3Cl_2 = 2FeCl_3.$$

Affinity for hydrogen

Chlorine has a great affinity for hydrogen, and both combines with it directly and removes it from many compounds, i.e. oxidizes them.

A mixture of chlorine and hydrogen will combine slowly in diffused daylight. In direct sunlight the combination occurs with explosive violence.

Hydrogen can be burnt in an atmosphere of chlorine. The gas is lit at a jet shaped as shown in fig. 41, and this is lowered into a gas jar full of chlorine. The hydrogen continues to burn.

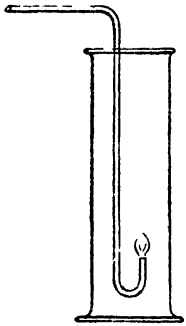


Fig. 41. — Burning Hydrogen in Chlorine

In both the above cases, hydrogen chloride is formed:

$$H_2 + Cl_2 = 2HCl.$$

Chlorine will remove the hydrogen from hydrogen sulphide (p. 181), forming hydrogen chloride and sulphur:

$$H_2S + Cl_2 = 2HCl + S.$$

To demonstrate this, a jar of hydrogen sulphide is inverted over a jar of chlorine. On removing the plates and allowing the gases to come into contact, clouds of sulphur are formed.

Hydrocarbons burn in chlorine, forming hydrogen chloride and liberating carbon in the form of soot. A gas jar full of chlorine is inverted over a burning candle. The candle continues to burn with a deep red flame and soot is deposited on the inside of the jar.

Another hydrocarbon which burns readily in chlorine is turpentine. This is usually shown by soaking a piece of

filter paper in turpentine and dropping it in a jar of chlorine. The turpentine may catch fire spontaneously and burn with a red flame, depositing soot in the jar. If difficulty is found in doing this satisfactorily — the turpentine may refuse to catch fire — the soaked filter paper may be carefully warmed before dropping it in the jar:

$$\underset{\text{(turpentine)}}{C_{10}H_{16}} + 8Cl_2 = 16HCl + 10C.$$

Ammonia is oxidized by chlorine to nitrogen:

$$2NH_3 + 3Cl_2 = 6HCl + N_2.$$

Sulphurous acid, H_2SO_3, made by dissolving sulphur dioxide in water, is oxidized by chlorine to sulphuric acid:

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl.$$

In all the above cases, then, chlorine is seen to possess a great affinity for hydrogen; it is a good oxidizing agent. Its oxidizing action, however, is also shown by its affinity for other electropositive elements.

When chlorine is bubbled through a solution of ferrous chloride, the green solution is turned yellow, ferric chloride being formed:

$$\underset{\substack{\text{(ferrous}\\ \text{chloride)}}}{2FeCl_2} + Cl_2 = \underset{\substack{\text{(ferric}\\ \text{chloride)}}}{2FeCl_3}.$$

Another important example of the oxidizing action of chlorine is that it displaces bromine and iodine, respectively, from solutions of bromides and iodides, when the gas is passed into solutions of these salts:

$$\underset{\substack{\text{(potassium}\\ \text{bromide)}}}{2KBr} + Cl_2 = \underset{\substack{\text{(potassium}\\ \text{chloride)}}}{2KCl} + \underset{\text{(bromine)}}{Br_2}.$$

The bromine appears as a red liquid, which is a solution of bromine in water. Some liquid bromine also is seen at the bottom of the test tube as a heavy dark red liquid.

The action with iodides is similar:

$$\underset{\text{(potassium iodide)}}{2KI} + Cl_2 = 2KCl + \underset{\text{(iodine)}}{I_2}.$$

Here the iodine colours the solution brown, and solid iodine is seen as a black solid at the bottom of the test-tube.

It must be repeated that the above reactions are oxidations, the chlorine removing the electropositive element (potassium) to liberate the bromine and iodine.

Reactions with alkalis

When passed into *cold dilute* solutions of alkalis, chlorine forms a mixture of chloride and **hypochlorite:**

$$Cl_2 + \underset{\text{(sodium hydroxide)}}{2NaOH} = NaCl + \underset{\text{(sodium hypochlorite)}}{NaClO} + H_2O.$$

$$Cl_2 + \underset{\text{(potassium hydroxide)}}{2KOH} = KCl + \underset{\text{(potassium hypochlorite)}}{KClO} + H_2O.$$

When chlorine is passed into *hot concentrated* solutions of alkalis, however, a mixture of chloride and **chlorate** is formed:

$$3Cl_2 + 6NaOH = 5NaCl + \underset{\text{(sodium chlorate)}}{NaClO_3} + 3H_2O.$$

$$3Cl_2 + 6KOH = 5KCl + \underset{\text{(potassium chlorate)}}{KClO_3} + 3H_2O.$$

Bleaching powder, or **chloride of lime,** is made by passing chlorine over dry slaked lime:

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O.$$

Bleaching powder is a useful source of chlorine, and being a solid it is easier to handle and transport than the gas or liquid.

Chlorine can be liberated from it by the action of acids:

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$
$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2.$$

Bleaching powder always smells of chlorine. This is due to carbonic acid (carbon dioxide plus water) in moist air reacting with it:

$$CaOCl_2 + \underset{\text{(carbonic acid)}}{H_2CO_3} = \underset{\text{(calcium carbonate)}}{CaCO_3} + H_2O + Cl_2.$$

Uses of chlorine

Chlorine is used as a bleach, both as gas and in the form of bleaching powder.

Use is also made of the fact that it is a germicide and disinfectant. A small amount of chlorine is added to drinking water to sterilize it, and larger amounts to water in swimming baths.

HYDROCHLORIC ACID

Hydrochloric acid, HCl, is a gas which is extremely soluble in water. Its composition shows that it is a compound of hydrogen and chlorine, that is, it is **hydrogen chloride.**

The gas is usually referred to as hydrogen chloride, while the solution in water is called hydrochloric acid. Hydrochloric acid is sometimes called *spirits of salt*; an old name for it is *muriatic acid.*

Laboratory preparation

Hydrochloric acid is formed by the action of concentrated sulphuric acid upon any chloride. Obviously, then, sodium chloride is used for the laboratory preparation, because this substance can be obtained very cheaply in the pure state.

The salt is put in a round-bottomed flask fitted with

a thistle funnel and delivery tubing (fig. 42). On adding concentrated sulphuric acid hydrogen chloride is evolved. No heat is required at first, but heat may be applied as the reaction slows down. Only one hydrogen atom of the dibasic sulphuric acid molecule is replaced by sodium:

$$NaCl + H_2SO_4 = \underset{\text{(sodium hydrogen sulphate)}}{NaHSO_4} + HCl.$$

acid salt

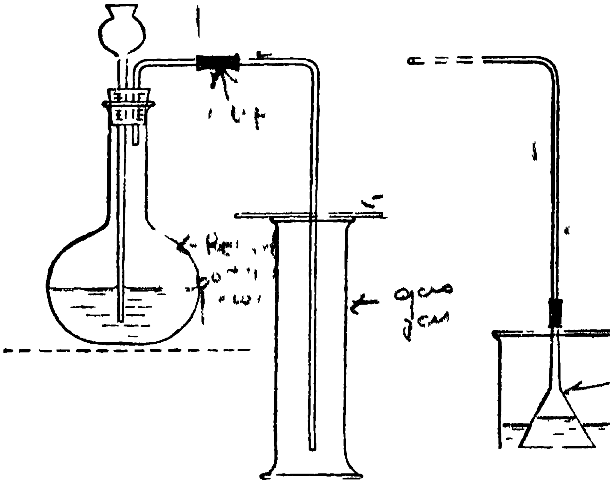


Fig. 42. — Preparation of Hydrogen Chloride Gas and Solution

(The full replacement of hydrogen is brought about by raising the temperature considerably, and this is done in the industrial preparation:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Here, obviously, twice as much hydrochloric acid is produced from the same quantity of sulphuric acid as at the lower temperature.)

The gas is collected in gas jars by upward displacement of air, using a cardboard cover to the gas jar as in the case of chlorine.

A solution is made by connecting the delivery tube to an inverted funnel, which dips in a beaker of water (fig. 42). This prevents the solution being sucked back into the flask; the gas is so soluble in water that if a delivery tube were to dip straight into the water, the gas would dissolve faster than it was evolved. When the funnel is attached, however, any attempt at this is frustrated, because the water level rising up the funnel makes the level in the beaker fall. When it falls below the rim of the funnel, air enters, and the water which has risen up drops back again.

Industrial preparation

Hydrochloric acid is prepared on the large scale in the manufacture of salt cake, anhydrous sodium sulphate, Na_2SO_4. Sodium hydrogen sulphate is first made by the action of sulphuric acid on common salt, without the application of heat:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The sodium hydrogen sulphate is then heated with more salt in a reverberatory furnace, when sodium sulphate is formed:

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The hydrochloric acid from the first stage of the process is purer than that from the second stage, the latter being mixed with furnace gases.

Pure hydrochloric acid is made by the direct combination of hydrogen and chlorine. These two gases are produced in the manufacture of sodium hydroxide by the electrolysis of brine. This method is superseding the other processes.

Properties

Hydrogen chloride is a colourless gas with a pungent smell. It does not burn or support burning. When

mixed with ammonia it forms dense white clouds of ammonium chloride:

$$NH_3 + HCl = NH_4Cl.$$

When it comes into contact with the air, hydrogen chloride forms steamy fumes. This is due to the formation of small droplets of hydrochloric acid, the gas dissolving in water present in the air.

It is extremely soluble in water, the solution being strongly acid. The fountain experiment (see p. 133) will work well with this gas, as it does with ammonia. In this case, however, the water in the vessel is coloured with blue litmus, which is turned red on entering the flask.

Hydrogen chloride solution is an acid; it has a sour taste, turns blue litmus red, dissolves a number of metals, reacts with bases to give salts (chlorides) and water, and reacts with carbonates, forming salts and giving off carbon dioxide.

Neither dilute nor concentrated hydrochloric acid will react with copper or lead.

Hydrochloric acid is oxidized by most oxidizing agents, chlorine being formed.

Tests for chlorides (including hydrogen chloride)

(1) To a portion of the suspected chloride in a test-tube, add some manganese dioxide and concentrated sulphuric acid. Evolution of chlorine (recognized by its smell and its bleaching action on litmus paper) indicates that the substance was a chloride. The sulphuric acid reacts with the chloride to give hydrochloric acid, which is immediately oxidized to chlorine by the manganese dioxide.

(2) To a solution of the suspected chloride add a little nitric acid and then silver nitrate solution. A white precipitate of silver chloride indicates the presence of a chloride in the original solution:

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$

Pour half the contents of the test-tube into another test-tube. To one sample add ammonium hydroxide and shake. The precipitate will dissolve. Shake the other up alone. The white precipitate will coagulate (congeal into lumps) and on exposure to light will gradually turn violet.

Composition of hydrogen chloride

A special tube is generally used for determining the volumetric composition of hydrogen chloride. It is made in two sections joined by a tap (fig. 43), the volume of one being twice that of the other. The two ends are closed by glass stoppers. The lower, larger portion of the tube is filled with hydrogen by downward displacement of air, and the upper portion filled with chlorine by upward displacement of air.

The communicating tap is then opened and the tube exposed to light, but not to direct sunlight. After a day or two the reaction will be complete. Make sure by putting the tube in sunlight; there will not be sufficient hydrogen and chlorine present to cause an explosion.

Fig. 43. — Apparatus for determining Composition of Hydrogen Chloride.

The tube is then placed with the longer portion downward and the end under dry mercury and the stopper is removed. No mercury is seen to enter, nor is gas seen to escape.

Water is then poured on to the mercury surface, and the tube lifted so that the open end is under water. The

water is seen to rise up and fill the lower part of the tube. The gas left in the upper part is found to be hydrogen.

From this it is seen that when hydrogen and chlorine combine, the volume of the hydrogen chloride formed is equal to the total volume of the gases which combine, since no change of volume occurred.

Also, since half the volume of hydrogen originally present was left over, equal volumes of hydrogen and chlorine combined.

That is, 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.

Since, by Avogadro's hypothesis, equal volumes of different gases contain the same number of molecules,

n molecules of hydrogen combine with n molecules of chlorine to form $2n$ molecules of hydrogen chloride;

$\therefore$ 1 molecule of hydrogen combines with 1 molecule of chlorine to form 2 molecules of hydrogen chloride.

Since 1 molecule of hydrogen contains 2 atoms, as does 1 molecule of chlorine, it follows that

2 molecules of hydrogen chloride contain 2 atoms of hydrogen and 2 atoms of chlorine,

$\therefore$ 1 molecule of hydrogen chloride contains 1 atom of hydrogen and 1 atom of chlorine;

Hence the formula for hydrogen chloride is HCl.

QUESTIONS

1. How would you prepare a few jars of chlorine in the laboratory?

2. What are the principal properties of chlorine?

3. How is chlorine prepared on the large scale? What are its chief uses?

4. Give three good reasons for classifying chlorine as an oxidizing agent.

5. What is bleaching powder? What are its uses? Why does it smell of chlorine?

6. How would you obtain (*a*) a few jars of hydrogen chloride, (*b*) a solution of hydrogen chloride in water?

7. Describe the industrial preparation of hydrochloric acid. What are its chief uses?

8. What are the chief properties of hydrogen chloride gas and solution?

9. A certain crystalline substance is said to be a chloride. What tests would you apply to confirm this?

10. Describe an experiment to verify that the formula for hydrogen chloride is HCl.

11. What weight of sulphuric acid is required to use up 50 gm. of common salt in preparing hydrochloric acid in the laboratory?

CHAPTER XVIII

BROMINE AND IODINE

The halogens

Chlorine belongs to a group of elements called the **halogens.** The word " halogen " means a salt producer, and you know that chlorine combines directly with metals, forming salts called chlorides. The other halogen elements do likewise.

The elements concerned are fluorine, chlorine, bromine, and iodine. They are often referred to as the *halogen family*; they show a family likeness in their properties and in the properties of their compounds.

We are not concerned at this stage with fluorine; chlorine we know in some detail; we shall now consider bromine and iodine.

BROMINE

Occurrence

This element does not occur in the free state, but it does so in combination as bromides in various parts of the world. Some bromides are present in sea water.

Preparation

In the same way that chlorine is prepared by the oxidation of hydrochloric acid, so bromine is prepared by the oxidation of hydrobromic acid. Manganese dioxide is likewise used as the oxidizing agent. You will not find a bottle of hydrobromic acid in the laboratory, as it is unstable, so bromine is generally prepared by heating a mixture of potassium bromide, manganese dioxide, and concentrated sulphuric acid in a retort. The potassium bromide and sulphuric acid form hydro-

bromic acid, which is immediately oxidized by the manganese dioxide to bromine:

$$2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2H_2O + Br_2.$$

The bromine distils over into the receiving flask as a dark red liquid.

Bromine is prepared on the large scale from the bromides occurring naturally in the Stassfurt deposits and elsewhere. Chlorine is passed through a hot concentrated solution of these salts, and displaces the bromine (see p. 158):

$$\text{e.g. } 2KBr + Cl_2 = 2KCl + Br_2.$$

Properties

Bromine is an abominably-smelling dark red volatile liquid. It boils at 59° C. and freezes readily on cooling. It is heavy for a non-metallic element, having a specific gravity of 3·2, and is the only element other than mercury which is a liquid at ordinary temperatures.

Bromine dissolves in water to some extent; the red solution is called *bromine water*.

Like chlorine, it combines directly with metals forming salts, called bromides, and it has a great affinity for hydrogen.

Hydrogen bromide

Bromine combines directly with hydrogen, but not so readily as chlorine: heating is necessary.

Hydrogen bromide cannot be prepared by a method similar to that for the preparation of hydrochloric acid, because the hydrogen bromide is somewhat unstable and reduces some of the sulphuric acid present to sulphur dioxide. It is generally prepared by the action of water on phosphorus tribromide, PBr_3.

$$PBr_3 + 3H_2O = \underset{\text{(phosphorous acid)}}{H_3PO_3} + 3HBr.$$

Care has to be taken because the reaction is violent. Some red phosphorus is mixed with water in a flask and bromine is dropped on to it from a dropping funnel. A violent reaction occurs as each drop falls, and hydrogen bromide is evolved and collected either as a gas or in solution, as in the case of hydrogen chloride.

Properties of hydrogen bromide

Hydrogen bromide is a colourless gas which fumes in air and is very soluble in water. It is denser than air. The solution in water is an acid, **hydrobromic acid**, which gives rise to a series of salts, **bromides.**

The bromides are similar to the chlorides, the most important being potassium bromide. Silver bromide, like silver chloride, is insoluble in water and nitric acid, but it dissolves *slightly* in ammonium hydroxide. (Silver chloride is readily soluble in ammonia.) Silver bromide is pale yellow in colour, and like silver chloride it darkens on exposure to light. It is used in photography.

IODINE

Occurrence

Iodine, like the other halogens, is not found in the free state in nature, but occurs widely as iodides. For example, iodides of sodium, potassium, and magnesium occur in sea water. Iodine is a necessary constituent of the human body. The thyroid gland, for example, contains iodine compounds, deficiency in which causes many diseases. These deficiencies may be made up by addition of iodides to the diet.

Laboratory preparation

Iodine may be prepared by heating a mixture of potassium iodide, manganese dioxide, and concentrated sulphuric acid in a retort. The potassium iodide and sulphuric acid give hydrogen iodide, which is oxidized

by the manganese dioxide to iodine. The total reaction is represented (cf. bromine, p. 168) by

$$2KI + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2H_2O + I_2.$$

Industrial preparation

Iodides are obtained from seaweed by mixing the ash (kelp) with water and separating out the other less soluble salts by concentrating the solution. The solution is treated with manganese dioxide and sulphuric acid and the iodine distilled off.

Iodine is also obtained from the sodium iodate occurring in the nitre deposits of Chile, after the sodium nitrate has been extracted. The crude sodium nitrate (caliche) contains 0·3 per cent of sodium iodate.

Properties

Iodine is a black crystalline solid, having a metallic appearance, although it is a non-metal. If heated it sublimes, that is, it changes directly from the solid to the vapour state, giving a beautiful violet vapour which solidifies in small crystals on a cool surface.

Iodine is moderately soluble in water, but dissolves readily in alcohol, giving the familiar brown solution, "tincture of iodine". It also dissolves in potassium iodide solution.

Iodine colours starch a deep blue colour, and this provides a good test for the element, as the reaction occurs with a very small quantity of iodine.

Hydrogen iodide

Iodine, like chlorine and bromine, combines directly with hydrogen to give hydrogen iodide, but with more difficulty than bromine. A catalyst is necessary.

Hydrogen iodide is decomposed even more easily than hydrogen bromide, and so cannot be prepared from sulphuric acid and an iodide.

It may be prepared in the laboratory by a method similar to that described for hydrogen bromide, namely, by the action of water on phosphorus tri-iodide. The phosphorus tri-iodide is made as required from red phosphorus and iodine:

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

Properties of hydrogen iodide

Hydrogen iodide is a heavy colourless gas which fumes in air and is very soluble in water, giving an acid solution. This acid solution is colourless, but is soon seen to turn brown. This is due to its unstable nature: it is oxidized to iodine, which causes the brown colour:

$$4HI + O_2 = 2H_2O + 2I_2.$$

The acid, **hydriodic acid**, gives rise to a series of salts, **iodides.** The most important is potassium iodide, a white crystalline solid similar to potassium chloride and potassium bromide. Silver iodide is, like silver chloride and silver bromide, insoluble in water and nitric acid, but is deep yellow in colour and is *insoluble* in ammonium hydroxide.

Let us now summarize some of the properties of the halogens. We can see the similarity between these elements and the gradation of properties, with bromine in the intermediate position between chlorine and iodine.

Chlorine is a gas, bromine a liquid, iodine a solid.

All are coloured: chlorine green, bromine dark red, iodine black (vapour violet).

All have a valency of 1.

All combine directly with hydrogen: chlorine very readily (explodes in sunlight), bromide on heating with hydrogen, iodine on heating with hydrogen in the presence of a catalyst.

Hydrogen chloride, hydrogen bromide, and hydrogen

iodide are all colourless gases which fume in air and are very soluble in water, giving a strongly acid solution.

Silver salts: all are insoluble in water and nitric acid. Silver chloride is white and is readily soluble in ammonium hydroxide; silver bromide is pale yellow and slightly soluble in ammonium hydroxide; silver iodide is deep yellow and insoluble in ammonium hydroxide.

QUESTIONS

1. What are the "halogen" elements? Why are they classed together as a "chemical family"?

2. How is bromine prepared in the laboratory? What are its chief properties?

3. Describe the preparation and properties of hydrogen bromide.

4. What are the chief properties and uses of iodine? How is it prepared on the large scale?

5. Three bottles each contain a white crystalline substance. One is potassium chloride, one potassium bromide, and one potassium iodide. What tests would you apply to enable you to label the bottles correctly?

CHAPTER XIX

SULPHUR: SULPHURIC ACID

Occurrence

Sulphur occurs in the free state in large quantities in Italy, notably in Sicily; and also in the United States, chiefly in Texas and Louisiana. In Italy the sulphur occurs in strata with rock, chiefly gypsum and limestone. The sulphur is generally supposed to have been formed by the reduction of gypsum by organic matter:

$$2CaSO_4 + 3C = 2CaCO_3 + CO_2 + 2S.$$

In Texas and Louisiana, where most of the sulphur now comes from, the element occurs at a depth of 500 ft. or more.

Extraction of sulphur

The Sicilian process. — This consists of building the crude sulphur and rock into heaps, with vertical air spaces left, and covering the heap with powdered sulphur ore. The heap is kindled at the top, and the heat of the burning sulphur causes the remainder to melt and this is run into wooden moulds. It may seem wasteful to use sulphur as fuel, but it is much more abundant and is cheaper than coal.

The crude sulphur thus obtained is shipped to Marseilles, where coal is cheaper, and is purified by distillation from iron retorts.

The vast American deposits, and the rapid and efficient method of extracting pure sulphur there, have rendered the Italian sulphur production relatively unimportant.

The Frasch process. — In America the deposit of

sulphur is far down below strata of clay, quicksand, and rock.

A boring is made down to the sulphur deposits, and a "sulphur pump", consisting of four concentric tubes, is sunk (fig. 44). Down the two outer pipes superheated water is passed. This water is kept at about 170° C. by compressing it to about 10 atmospheres. This superheated water is hot enough to melt the sulphur, and

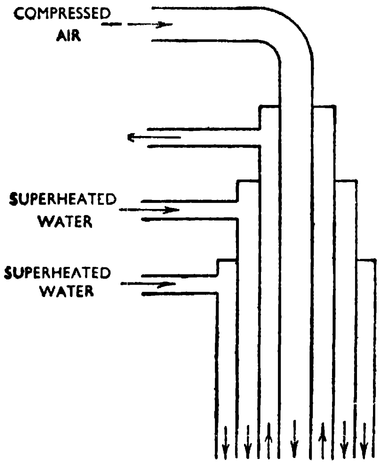


Fig. 44. — Extraction of Sulphur — Frasch Process

compressed air forced down the central tube forces the mixture of water and molten sulphur up the pipe next to it. This frothy mixture passes into immense wooden vats, where the sulphur solidifies; when the walls of a vat are removed, a great hill of sulphur remains. This is of so high a degree of purity that no further refinement is necessary. The output is tremendous: a single pump often produces as much as 500 tons of sulphur a day.

It is easy to see, then, that this process is more important than the Sicilian process: 80 per cent of the sulphur used comes from America.

The allotropic forms of sulphur

Sulphur is found to exist in different forms; these different forms of the same element exhibit different properties. When an element behaves in this way, it is said to exhibit **allotropy,** and the different forms of the element are called **allotropic forms.**

The chief crystalline forms of sulphur are **rhombic sulphur** and **monoclinic sulphur.** Amorphous (i.e. non-crystalline) sulphur also exists, one interesting form being **plastic sulphur.**

Rhombic or octahedral sulphur (α-sulphur)

Ordinary crystalline sulphur consists of rhombic crystals (fig. 45). Shapely crystals can be obtained by dissolving ordinary roll sulphur in carbon disulphide, and allowing the liquid to evaporate slowly in the fume cupboard. No flame should be in the vicinity, as carbon disulphide is extremely inflammable.

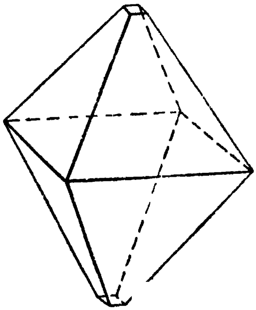


Fig. 45. — Rhombic Sulphur

Rhombic sulphur consists of transparent yellow rhombic crystals, with a specific gravity of 2·06 and a melting-point of 113° C. It is soluble in carbon disulphide, but insoluble in water. Rhombic sulphur is stable at ordinary temperatures.

Monoclinic or prismatic sulphur (β-sulphur)

This allotropic form of sulphur is produced when melted sulphur is allowed to crystallize.

Place plenty of roll sulphur, crushed up, in an evaporating dish and heat it slowly until all the sulphur has melted, and then allow it to cool. As soon as a crust has

formed all over the surface, pierce two holes in it and quickly pour the still liquid sulphur out of one hole. Cold air enters the other hole and quickly cools liquid sulphur from just above the melting-point. Crystals of monoclinic sulphur are formed. On removing the top crust, the crystals below may be seen, and are found to be long transparent pale yellow needle-shaped crystals (fig. 46).

Monoclinic sulphur has a density of 1·96 and a melting-point of 119° C. Like rhombic sulphur, it is insoluble in water and soluble in carbon disulphide, but on crystallizing from solution it forms rhombic crystals. It is unstable: if the crystals formed as described are

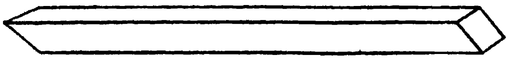


Fig. 46. — Monoclinic Sulphur

left for a day or two, they become opaque, somewhat lighter in colour, and brittle, and on examination are found to have become aggregations of small rhombic crystals. The shape of the mass is still that of the original monoclinic crystals.

Plastic sulphur

This is an amorphous form of sulphur, and is made by rapidly cooling sulphur from the boiling-point or near it.

Some sulphur is melted in a test-tube and heated until it is boiling rapidly. It is then poured in a thin stream into a beaker of cold water, when it forms yellow or brown transparent threads with a consistency like that of rubber. When freshly made, it is insoluble in carbon disulphide.

Plastic sulphur is unstable, becoming brittle after a few days and reverting principally to rhombic sulphur.

Liquid sulphur can exist in different forms, and it is interesting to heat sulphur slowly from melting-point to boiling-point and watch the changes that occur.

The sulphur melts to form an amber-coloured mobile liquid. On further heating it becomes darker in colour, and at 160° C. it suddenly becomes very viscous, so much so that the test-tube may be inverted without any liquid falling out. It is by now reddish-brown in colour. On continuing to heat, the sulphur is seen to become darker in colour and more mobile, until at 444° C. it begins to boil, giving off a yellowish-brown vapour.

On cooling the reverse changes are observed.

Chemical properties of sulphur

Sulphur burns in air with a weak blue flame, forming sulphur dioxide, a pungent-smelling gas:

$$S + O_2 = SO_2.$$

The chemical properties of sulphur are seen to bear a strong resemblance to those of oxygen. There is the "family likeness" that we observed in the case of the halogens. For this and for other reasons, the two elements are classed as belonging to the same chemical family.

As oxygen combines with many metals and non-metals, forming oxides, so sulphur combines with many elements, forming **sulphides**.

If hydrogen is passed through boiling sulphur, hydrogen sulphide, an unpleasant-smelling gas, is formed:

$$H_2 + S = H_2S \quad \text{(compare } H_2O\text{)}.$$

Sulphur can be made to combine with carbon, forming carbon disulphide, CS_2, by passing sulphur vapour over red-hot carbon:

$$C + 2S = CS_2 \quad \text{(compare } CO_2\text{)}.$$

Metals, however, combine more readily with sulphur than non-metals do.

Heat a mixture of iron filings and sulphur gently in a crucible. Soon a vigorous reaction is observed, ferrous sulphide being formed:

$$Fe + S = FeS.$$

Heat a small spiral of copper wire and plunge it, red hot, into the vapour in a test-tube containing boiling sulphur. The copper burns brightly, forming cuprous sulphide:

$$2Cu + S = Cu_2S.$$

Uses of sulphur

Sulphur is used for making sulphuric acid, matches, and dyes. A large quantity of sulphur is used for vulcanizing rubber. Rubber in its untreated state is not suitable for use, but when heated with sulphur, a process known as vulcanization, it produces the useful substance we know.

Hydrogen sulphide (sulphuretted hydrogen), H_2S

Hydrogen sulphide is generally prepared in the laboratory by the action of dilute hydrochloric or sulphuric acid on ferrous sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S.$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Water and ferrous sulphide are placed in a Woulfe bottle, and concentrated acid is poured down the thistle funnel. The gas may be collected over warm water (fig. 47), or, if you like the smell, by upward displacement of air.

It is usual to have hydrogen sulphide " on tap " in the laboratory, and for this purpose it is usually generated in a Kipp's apparatus, or other device, to be found in the fume cupboard. The Kipp's apparatus (fig. 48) works in the following way:

On opening the tap, the acid comes into contact with

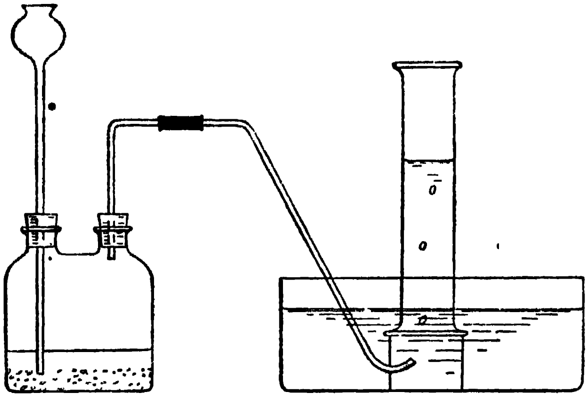


Fig. 47. — Preparation of Hydrogen Sulphide

the ferrous sulphide, and hydrogen sulphide is evolved. On closing the tap, the hydrogen sulphide, still being given off and unable to escape by way of the tap, forces

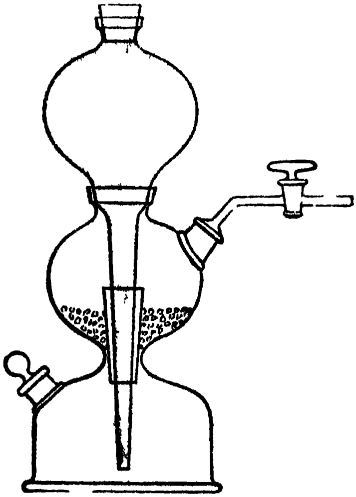


Fig. 48. — Kipp's Apparatus

the acid away from the ferrous sulphide and up the central tube to the upper bulb. The evolution of gas stops when there is no more acid in contact with the sulphide, and the central bulb is full of the gas ,ready to be bubbled where required when the tap is opened.

A useful substitute may be made by joining two aspirator bottles as in fig. 49. One contains the dilute acid, and the other ferrous sulphide, the latter being kept on

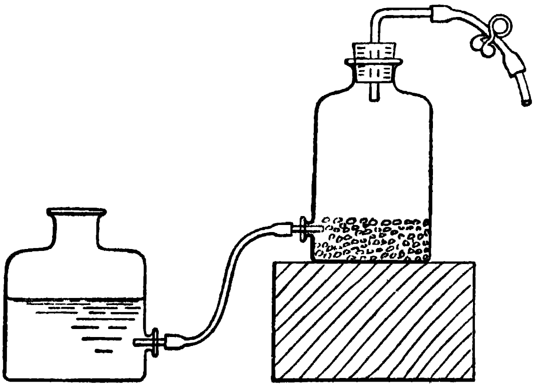


Fig. 49. — Alternative Hydrogen Sulphide Generator

a support above the level of the acid in the other bottle. On lowering the ferrous sulphide bottle and opening the pinch cock, the gas is evolved.

Properties. — Hydrogen sulphide is a colourless gas with a powerful, unpleasant, sweetish odour, like that of rotten eggs. In fact, this gas is produced when eggs decay. The gas is poisonous, causing headache when inhaled even in small quantities.

Hydrogen sulphide burns with a blue flame in air. With a plentiful supply of oxygen, sulphur dioxide is formed:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

With a limited supply of air, however, sulphur is deposited:

$$2H_2S + O_2 = 2H_2O + 2S.$$

Hydrogen sulphide is fairly soluble in water: at ordinary temperatures water dissolves approximately three times its volume of the gas. The solution is found to turn blue litmus red, showing that it is an acid. The solution is sometimes referred to as "hydrosulphuric acid". It is an extremely weak acid.

Hydrogen sulphide is a reducing agent.

Sulphuric acid is reduced to sulphur dioxide, and the hydrogen sulphide simultaneously oxidized to sulphur:

$$H_2S + H_2SO_4 = 2H_2O + SO_2 + S.$$

Nitric acid is similarly reduced to nitrogen peroxide:

$$H_2S + 2HNO_3 = 2H_2O + 2NO_2 + S.$$

The halogens are reduced to the halide acids. This is done by passing hydrogen sulphide through chlorine water, bromine water, or water containing iodine in suspension. In each case the hydrogen sulphide is oxidized to sulphur, which is deposited:

$$Cl_2 + H_2S = 2HCl + S.$$
$$Br_2 + H_2S = 2HBr + S.$$
$$I_2 + H_2S = 2HI + S.$$

Precipitation of sulphides from solutions of salts

The importance of hydrogen sulphide in the laboratory is due to the fact that when it is passed through solutions of salts, sulphides are formed. Most of these sulphides are insoluble and are therefore precipitated. Moreover, they can be grouped, and many are distinctive; hence formation of the sulphide is of great help in analysis.

For example, lead, copper, and bismuth sulphides are formed as black precipitates when hydrogen sulphide

is bubbled through solutions of their salts. They are insoluble in acid solution.

Zinc and manganese sulphides are soluble in acid solution, but are precipitated from neutral or alkaline solution. Zinc sulphide is white and manganese sulphide flesh-coloured.

OXIDES OF SULPHUR

Sulphur dioxide, SO_2

Burning sulphur has been used from very ancient times for fumigation and bleaching. Lavoisier in 1777 showed that the gas formed is an oxide of sulphur.

Preparation. — Sulphur dioxide is, as we have seen, formed when sulphur burns in air. It is generally prepared in the laboratory, however, by heating concentrated sulphuric acid with copper:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Copper turnings are placed in a round-bottomed flask fitted with thistle funnel and delivery tubing joined to a Woulfe bottle containing concentrated sulphuric acid to dry the gas. The gas is led to a gas jar, where it is collected by upward displacement of air (fig. 50). Concentrated sulphuric acid is poured down the funnel, and the flask is gently heated until the contents are effervescing readily. A dark brown mixture is left in the flask. This consists of anhydrous copper sulphate (white) mixed with copper sulphide (black), the latter formed by a side reaction not indicated in the equation.

Other substances could be used instead of copper: for example, mercury, silver, sulphur, and carbon:

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2.$$
$$S + 2H_2SO_4 = 2H_2O + 3SO_2.$$
$$C + 2H_2SO_4 = 2H_2O + CO_2 + 2SO_2.$$

On the large scale sulphur dioxide is prepared by burning sulphur or iron pyrites or "spent oxide" from the gas works in air:

$$S + O_2 = SO_2.$$
$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

Atmospheric nitrogen is, of course, present with the sulphur dioxide prepared in this way.

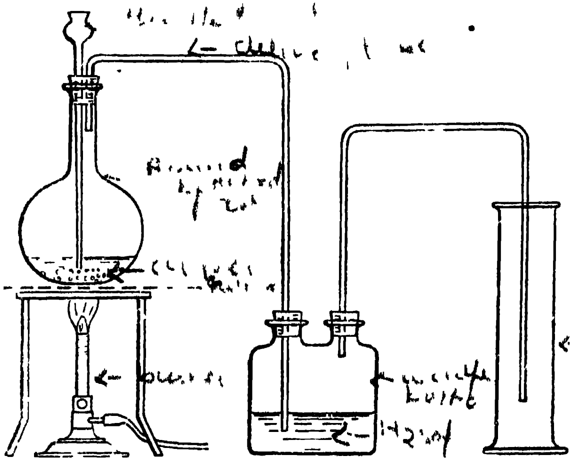


Fig. 50. — Preparation of Sulphur Dioxide

Properties. — Sulphur dioxide is a colourless gas with a pungent smell like that of burning sulphur, which is natural, since, when sulphur burns in the air, sulphur dioxide is formed. Sulphur dioxide can easily be liquefied under pressure, giving a colourless liquid. The gas is denser than air, and will not burn or support combustion. Sulphur dioxide bleaches many colouring matters.

When sulphur dioxide is passed through a solution of potassium permanganate, the purple solution is decolorized:

$$2KMnO_4 + 5SO_2 + 2H_2O$$
$$= K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

When the gas is passed through a solution of potassium dichromate, acidified by the addition of a little sulphuric acid, or if a piece of filter paper is dipped into acidified potassium dichromate solution and exposed to the gas, it is turned from yellow to green. This is due to the formation of green chromium sulphate:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \\ = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

This is used as a test for the gas.

Sulphur dioxide dissolves in water readily, forming sulphurous acid:

$$SO_2 + H_2O = H_2SO_3.$$

Sulphurous acid, H_2SO_3

Sulphurous acid exists only in solution, and cannot be obtained free. If we attempt to concentrate a solution, sulphur dioxide is given off. Its salts, however, are readily obtained. They are called **sulphites**, and the most important is sodium sulphite, Na_2SO_3.

The acidic nature of a solution of sulphur dioxide is shown by the facts that it turns blue litmus red, and forms a salt and carbon dioxide with carbonates. For example:

$$Na_2CO_3 + H_2SO_3 = Na_2SO_3 + H_2O + CO_2.$$

Sulphurous acid also reacts with alkalis, giving a salt and water. This is best shown by passing sulphur dioxide into a solution of sodium hydroxide, when it forms sodium sulphite and water:

$$2NaOH + SO_2 = Na_2SO_3 + H_2O.$$

On continuing to pass the gas, however, sodium hydrogen sulphite (sodium bisulphite) is formed:

$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3.$$

If this sodium hydrogen sulphite solution is mixed with the correct amount of sodium hydroxide (an amount equal to that started with before passing in the sulphur dioxide) the normal sulphite is formed:

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

In this way sodium sulphite may be prepared in the laboratory. The reason for this round-about way is that although sodium sulphite is formed initially on passing sulphur dioxide through the sodium hydroxide solution, there is no indication as to when the reaction is complete. If the gas is not passed in for a sufficient time, some sodium hydroxide will also be present; if foı too long, some sodium bisulphite will be formed. Therefore the sodium hydroxide is saturated with sulphur dioxide, when only sodium hydrogen sulphite is formed, and then a quantity of sodium hydroxide equal to that started with is added.

Bleaching action of moist sulphur dioxide

Sulphur dioxide, in the presence of moisture, is found to bleach many substances. It is interesting to compare the bleaching action of this gas with that of moist chlorine, which was seen to be an oxidation (see p. 155). Sulphurous acid, however, is a reducing agent, being itself readily oxidized to sulphuric acid, and its bleaching action is due to the reduction of the colouring matter to a colourless substance.

An advantage of moist sulphur dioxide is that it can be used to bleach substances which would be spoilt by chlorine. Silks, for example, can be safely bleached by sulphur dioxide. The moist gas is also used to bleach the straw used for making Panama hats; the straw would be rotted by chlorine.

A disadvantage of sulphur dioxide as a bleaching agent is that the bleaching is not so permanent; the bleached matter slowly oxidizes in the air, particularly in sun-

light. The bleached straw of Panama hats gradually resumes its yellow colour as the oxidation takes place.

Composition of sulphur dioxide

A small piece of sulphur is placed in a metal spoon in dry oxygen over mercury in an apparatus shaped as in fig. 51. The sulphur is ignited by passing a current of electricity through the fine platinum wire touching the sulphur. When the sulphur has burnt and the apparatus has cooled to room temperature again, the volume is found to be unchanged.

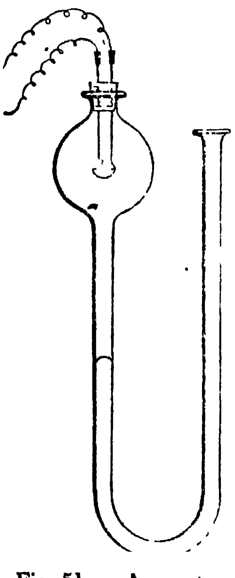


Fig. 51. — Apparatus for determining the Composition of Sulphur Dioxide

That is, the sulphur dioxide formed contains its own volume of oxygen.

Then, by Avogadro's hypothesis, since 1 volume of sulphur dioxide contains 1 volume of oxygen,

1 *molecule* of sulphur dioxide contains 1 *molecule* of oxygen.

The vapour density of sulphur dioxide is found to be 32, and so its molecular weight is 64.

This contains 1 molecule of oxygen $(2 \times 16) = 32$.

$\therefore$ Weight of sulphur in the molecule $= 64 - 32 = 32$.

Since the atomic weight of sulphur is 32, a molecule of sulphur dioxide contains 1 atom of sulphur (S) and 1 molecule of oxygen (O_2).

Hence the formula for sulphur dioxide is SO_2.

Sulphur trioxide, SO_3

Sulphur trioxide is generally prepared by passing a mixture of dry sulphur dioxide and dry oxygen over a heated catalyst, platinized asbestos generally being used.

Sulphur trioxide is a colourless crystalline solid with a very strong affinity for water. It dissolves in water with extreme violence, forming sulphuric acid.

SULPHURIC ACID, H_2SO_4

Industrial preparation

(*a*) The contact process

The Contact Process is the simpler of the two main methods by which sulphuric acid is manufactured.

A mixture of sulphur dioxide, oxygen, and nitrogen, produced by burning sulphur or iron pyrites in excess of air, is dried and purified and passed over the catalyst, heated platinum, when the sulphur dioxide and oxygen combine to form the trioxide:

$$2SO_2 + O_2 = 2SO_3.$$

In the **Badische Process** the mixture of gases passes into an iron cylinder in which are vertical tubes packed with platinized asbestos. These are heated to start with, and the sulphur dioxide and air mixture is passed around them (fig. 52). The hot gases then pass down the tubes containing the catalyst, when combination takes place. Only initial heating of the catalyst is necessary, since once the reaction has got going, sufficient heat is evolved for the process to continue.

In another process, the **Grillo Process,** the catalyst is prepared by heating Epsom salt (magnesium sulphate, $MgSO_4 \cdot 7H_2O$) moistened with a solution of platinic chloride, $PtCl_4$. The salt loses its water of crystallization and swells up into a porous mass, and the platinic

chloride decomposes, the platinum formed being deposited on the very large surface of the anhydrous magnesium sulphate. The catalyst is placed on shelves in a converter and the gases are passed over. Once more, only initial heating is necessary.

The sulphur trioxide formed in the contact processes is not passed straight into water, because the violence of the combination causes a fog of very fine droplets of sulphuric acid to be formed, but it is absorbed in highly

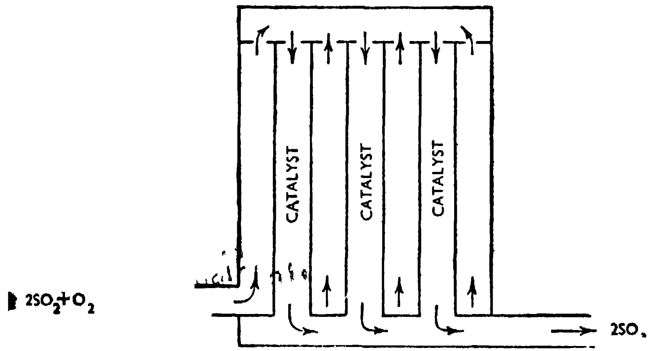


Fig. 52. — Contact Process. Badische Converter

concentrated sulphuric acid, water being added continuously as the sulphur trioxide is absorbed.

$$SO_3 + H_2O = H_2SO_4.$$

It is of great importance in the contact process to have the sulphur dioxide and oxygen pure, otherwise the catalyst is affected and its efficiency impaired; it is said to be " poisoned ".

The contact process produces sulphuric acid of a very high degree of purity, but it is more costly than the Chamber Process, by which somewhat less pure acid is prepared.

(*b*) The chamber process

In this process also sulphur dioxide is oxidized by atmospheric oxygen, but the catalyst consists of oxides of nitrogen.

The catalytic action of the oxides of nitrogen is due to nitric oxide acting as an "oxygen carrier". Nitric oxide is made either by the oxidation of ammonia (p. 143) or by one of various other methods, and this is oxidized by the oxygen of the air to nitrogen peroxide:

$$2NO + O_2 = 2NO_2.$$

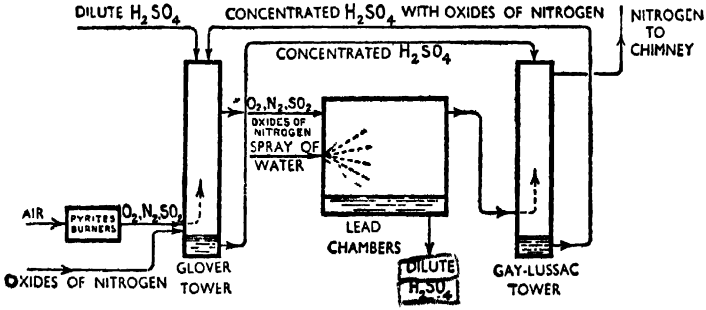


Fig. 53. — The Lead Chamber Process

The nitrogen peroxide gives up its extra oxygen to the sulphur dioxide to form sulphur trioxide, which with the spray of water forms sulphuric acid. The nitrogen peroxide is reduced back to nitric oxide:

$$NO_2 + H_2O + SO_2 = H_2SO_4 + NO.$$

Excess of air is passed over the iron pyrites or sulphur burners, resulting in sulphur dioxide being formed, together with oxygen and nitrogen from the air. These, along with oxides of nitrogen, pass up the Glover tower (fig. 53). This is a lead tower, covered inside with acid-resisting bricks and packed with flints or acid-resisting tiles. Down this trickles a mixture of dilute

sulphuric acid (chamber acid — see below) and concentrated sulphuric acid containing oxides of nitrogen in solution. This comes from the bottom of the Gay-Lussac tower (see below), which is constructed in much the same way as the Glover tower.

In the Glover tower the ingoing gases extract the oxides of nitrogen from the descending acid, and the mixture of gases, oxygen, nitrogen, sulphur dioxide, and oxides of nitrogen, passes into a series of lead chambers. Here a spray of water is blown in and sulphuric acid is formed and collects on the floor of the chambers. It is called **chamber acid,** and is 65–70 per cent sulphuric acid.

The gases emerging from the lead chambers, consisting mainly of oxides of nitrogen and atmospheric nitrogen, pass up the Gay-Lussac tower, down which concentrated sulphuric acid trickles. This dissolves the oxides of nitrogen, and the nitrogen passes into the chimney. The concentrated acid, charged with the recovered oxides of nitrogen, passes now to the top of the Glover tower, where the incoming gases take out the oxides of nitrogen, as we have seen.

The acid is concentrated in various ways. In one method the chamber acid is sprayed down a brick tower up which hot gases from a coke furnace are passing.

The lead chamber process is clumsy and produces rather impure acid, but it is cheaper than the contact process, and chamber acid has a ready sale where pure acid is not required.

Properties of sulphuric acid

Sulphuric acid is a dense, syrupy colourless liquid. One outstanding property is its great affinity for water, which it absorbs with the evolution of much heat. In diluting the acid, the acid should always be added slowly to the water, stirring the while. Never add water to the concentrated acid. Because of its affinity for water, concentrated sulphuric acid is a useful drying agent.

An interesting example of its affinity for water is shown in its action upon certain organic compounds, from which it removes the elements of water. If concentrated sulphuric acid is added to some moistened sugar in a beaker, the sugar immediately blackens, swells up to a frothy mass, and finally leaves a porous mass of carbon, smelling of burnt sugar. Sugar has the formula $C_{12}H_{22}O_{11}$, and the sulphuric acid removes the $11H_2O$:

$$C_{12}H_{22}O_{11} \underset{(H_2SO_4)}{=} 11H_2O + 12C.$$

Paper, which is a compound of carbon, hydrogen, and oxygen, similarly has the elements of water removed from it by concentrated sulphuric acid, carbon being left.

Sulphuric acid is a dibasic acid, giving rise to two series of salts, normal salts and acid salts, according as two or one hydrogen atoms in the molecule are replaced by a metal.

H_2SO_4	Sulphuric acid, or hydrogen sulphate.
$NaHSO_4$	Sodium hydrogen sulphate, or acid sodium sulphate.
Na_2SO_4	Sodium sulphate, or normal sodium sulphate.

Most sulphates are soluble in water. Barium sulphate, however, is insoluble, and its formation as a precipitate is used as a test for sulphates. To the suspected liquid add dilute hydrochloric acid and then some barium chloride solution. A white precipitate indicates the presence of sulphuric acid or a sulphate.

Other salts (for example, carbonates, sulphites, and phosphates) give white precipitates with barium chloride, but they are soluble in dilute hydrochloric acid, which explains why this acid is first added in the test.

Uses of sulphuric acid

Sulphuric acid has a vast number of uses. It is used in the preparation of hydrochloric acid and nitric acid,

in the manufacture of fertilizers (e.g. "superphosphate" and ammonium sulphate), in paper refining, for storage cells, for "pickling" iron (i.e. cleaning iron prior to coating with tin), and in making a vast number of explosives, dyes, and other chemicals.

QUESTIONS

1. Describe the extraction of sulphur by the Frasch process

2. Describe the changes which occur when sulphur is slowly heated until the liquid boils, and is then allowed to cool.

3. What do you understand by *allotropy*? How would you demonstrate that sulphur exhibits this phenomenon?

4. Describe the preparation of (*a*) monoclinic sulphur, (*b*) crystals of rhombic sulphur, (*c*) plastic sulphur.

5. State the principal properties of sulphur. Give reasons for classing it with oxygen as a member of the same "chemical family".

6. How is hydrogen sulphide prepared in the laboratory? Describe an apparatus in which the gas can be ready for use when required.

7. What are the principal properties of hydrogen sulphide? Explain the importance of hydrogen sulphide in qualitative analysis.

8. How is sulphur dioxide prepared in the laboratory? What are its chief properties?

9. How would you prepare crystals of sodium sulphite in the laboratory?

10. Describe the bleaching action of moist sulphur dioxide. In what ways does it differ from that of moist chlorine?

11. Give reasons for assuming that the formula for sulphur dioxide is SO_2.

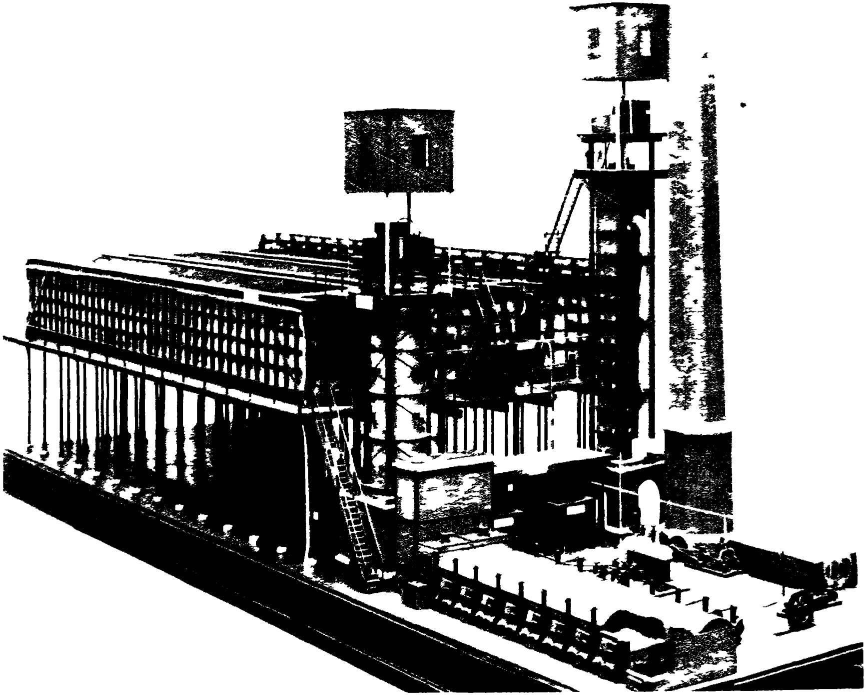
12. Describe the Contact process for the manufacture of sulphuric acid.

13. Describe the Chamber process for the manufacture of sulphuric acid.

14. What are the principal properties and uses of sulphuric acid?

15. What weight of sulphuric acid could be made from a ton of sulphur?

MODEL OF SULPHURIC
ACID CHAMBER PLANT



F 981

CHAPTER XX

PHOSPHORUS

Occurrence

Phosphorus was discovered by a German chemist, **Brand**, who obtained it by distilling evaporated urine, which contains phosphates, with sand and charcoal. Scheele prepared it from bone ash in 1771, after another Swedish chemist, Gahn, had shown that bones contain a large quantity of calcium phosphate.

Lavoisier, in 1774, showed that phosphorus is an element. Phosphorus does not occur in the free state, but does so in combination as phosphates in bones and many minerals.

Preparation

Calcium phosphate is crushed and mixed with sand and coke and fed into a furnace heated by an electric arc between two carbon rods (fig. 54, p. 194).

This is not a case of electrolysis; the electric arc merely supplies the heat necessary for the reaction.

The sand contains silica (silicon dioxide, SiO_2) and this forms calcium silicate, which is fusible and can be drawn off as a slag. (See Smelting of Iron, p. 257.) The reaction is

$$\underset{\substack{\text{(calcium}\\\text{phosphate)}}}{Ca_3(PO_4)_2} + \underset{\text{(silica)}}{3SiO_2} = \underset{\substack{\text{(calcium}\\\text{silicate)}}}{3CaSiO_3} + \underset{\substack{\text{(phosphorus}\\\text{pentoxide)}}}{P_2O_5}.$$

The phosphorus pentoxide is immediately reduced by the carbon (coke), forming phosphorus and carbon monoxide:

$$P_2O_5 + 5C = 2P + 5CO.$$

The phosphorus vapour and carbon monoxide are led under water, where the phosphorus solidifies in moulds, forming sticks of white phosphorus.

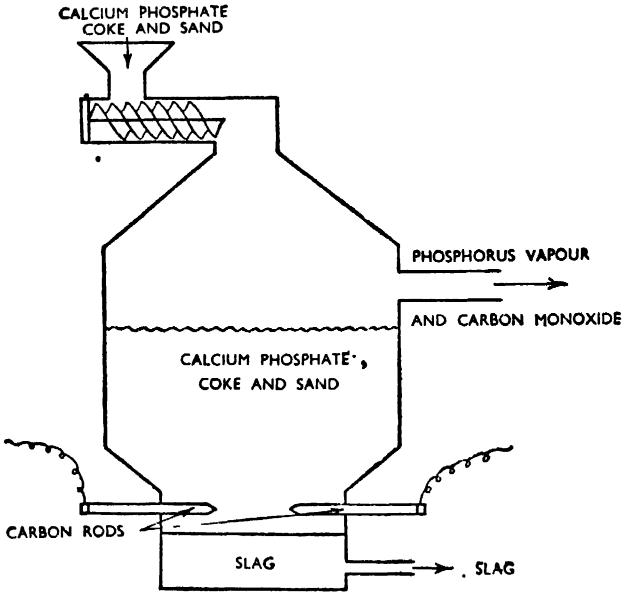


Fig. 54. — Manufacture of Phosphorus

Properties

Phosphorus exists in different allotropic modifications, the two most important forms being **white phosphorus** and **red phosphorus.**

White Phosphorus (also called yellow phosphorus)

This is a pale yellow (white when pure) translucent solid of waxy appearance. It is crystalline in form, and is moderately soft: it can be cut with a knife.

Perhaps its two most distinctive properties are that it glows in the air, and catches fire spontaneously. The

glow is a chemical characteristic — not physical, as in most cases of phosphorescence. It is a slow combustion, forming oxides.

At about 30° C. phosphorus catches fire and burns vigorously, giving off dense white fumes which consist chiefly of phosphorus pentoxide. White phosphorus is always kept under water, and should be touched only

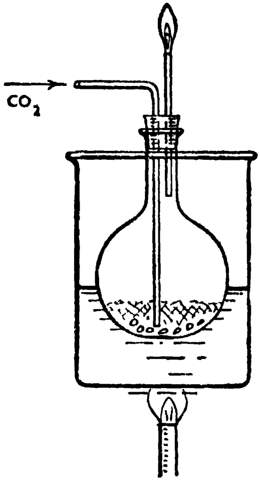


Fig. 55. — Phosphorus " Cold Flame "

with wet hands, if at all; phosphorus burns are very difficult to heal.

The glow of phosphorus may be demonstrated by means of an experiment (fig. 55). A few pieces of dry phosphorus are placed in a dry flask and covered with glass wool. The flask is heated gently over a water bath, carbon dioxide being passed through all the time. The phosphorus vapour cannot burn in the vapour of carbon dioxide, but does so as soon as it reaches the air. The flame is green and is so cool that the hand may be held in it.

White phosphorus is very slightly soluble in water, but is readily soluble in carbon disulphide. From the solution large transparent crystals can be obtained, if the solution is evaporated slowly in the dark and out of contact with the air. If a piece of filter paper is dipped into the solution of phosphorus in carbon disulphide, it will ignite spontaneously as soon as the solvent has evaporated, owing to the large surface of the finely divided crystals of phosphorus coming into contact with the air.

White phosphorus is extremely poisonous, and for that reason it is no longer used in the manufacture of matches. Constant exposure to the fumes of phosphorus causes rotting of the bones of the nose and jaws — " phossy jaw ".

Red phosphorus, once thought to be amorphous, is actually composed of very small crystals. It is formed by heating the white form in an atmosphere of carbon dioxide or nitrogen. (The white form may be obtained from the red by heating the latter in an inert atmosphere until it vaporizes, and quickly cooling the vapour.)

Red phosphorus is denser than the white form, their specific gravities being 2·20 and 1·83 respectively. Unlike white phosphorus, it is insoluble in carbon disulphide, does not glow or catch fire spontaneously in air or chlorine, and is non-poisonous.

Red and white phosphorus may be shown to be forms of the same element by converting a weighed amount of each into a compound, for example, the pentoxide. The same amount of pentoxide is formed in each case.

Phosphine, PH_3

This poisonous gas is prepared by heating white phosphorus with sodium hydroxide solution in an inert atmosphere:

$$4P + 3NaOH + 3H_2O = \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2} + PH_3.$$

A few small pieces of white phosphorus are placed in a round-bottomed flask and covered with sodium hydroxide solution. A delivery tube leads to a vessel of water, but no gas jar, as the gas is not collected (fig. 56). Coal gas is passed through the apparatus, and when the air has been swept out, the flask is heated. Phosphine is evolved, and each bubble, as it reaches the air, burns brightly with a yellow flame, and produces a white vortex ring of phosphorus pentoxide.

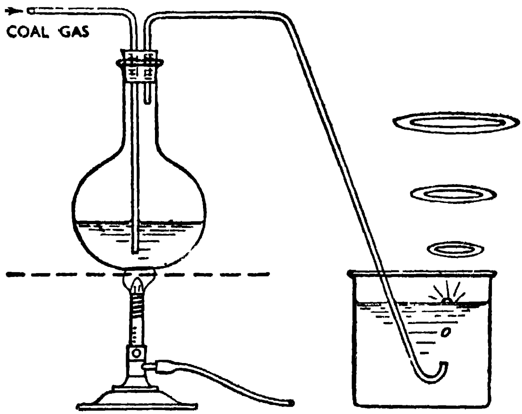


Fig. 56. — Preparation of Phosphine

Phosphine is also formed by the action of water on calcium phosphide:

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3.$$

" Holmes signals ", often attached to lifebuoys, contain calcium phosphide and calcium carbide. When the canister is pierced phosphine and acetylene are evolved, and the phosphine, igniting spontaneously, causes the acetylene to burn.

Properties. — Phosphine is a very poisonous colourless gas with a distinctive smell of decaying fish. When perfectly pure, the gas is not spontaneously inflammable

in air; the fact that the gas as usually prepared does so is due to the presence of small quantities of another hydride of phosphorus.

Phosphine bears some resemblance to ammonia. This is shown in its formula, and in the formation of *phosphonium salts*, similar to ammonium salts, e.g.

$$PH_3 + HCl = \underset{\text{(phosphonium chloride)}}{PH_4Cl}.$$

Compare $$NH_3 + HCl = NH_4Cl.$$

Phosphine, however, is only sparingly soluble in water, and the solution does not show any alkaline properties; no base which could be called phosphonium hydroxide is known.

Chlorides of phosphorus

White or red phosphorus combines directly with chlorine to form chlorides, phosphorus trichloride, PCl_3, and phosphorus pentachloride, PCl_5.

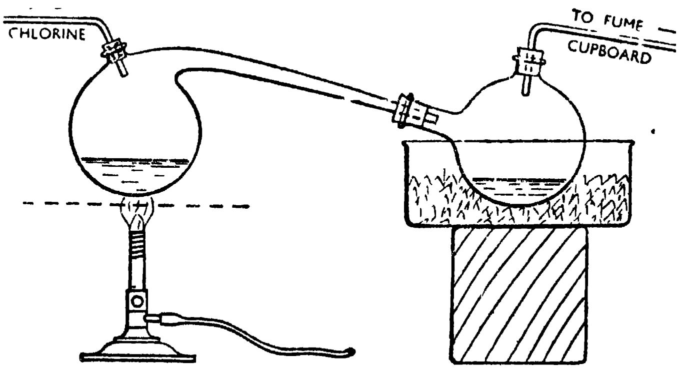


Fig. 57. — Preparation of Phosphorus Trichloride

Phosphorus trichloride, PCl_3, is formed by passing dry chlorine over heated phosphorus:

$$2P + 3Cl_2 = 2PCl_3.$$

The phosphorus is placed in a retort and a stream of chlorine is passed over. The phosphorus is then gently heated. The mouth of the retort leads to a cooled receiving flask (fig. 57). The phosphorus trichloride collects in the flask as a fuming colourless liquid.

Phosphorus pentachloride, PCl_5

The pentachloride, a yellow solid, is prepared by the action of chlorine on the trichloride.

A wide-necked flask is fitted with a dropping funnel and delivery tubes as shown in fig. 58, and dry chlorine

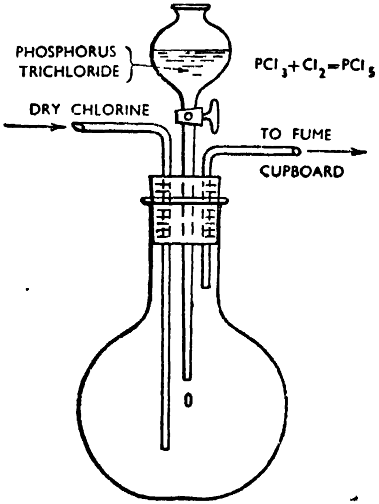


Fig. 58. — Preparation of Phosphorus Pentachloride

is passed through. The flask is kept cool, and phosphorus trichloride is allowed to drop in slowly. A vigorous reaction occurs as each drop of liquid enters the atmosphere of chlorine, and solid phosphorus pentachloride collects at the bottom of the flask.

Both the trichloride and pentachloride are attacked vigorously by water:

$$PCl_3 + 3H_2O = \underset{\text{(phosphorous acid)}}{H_3PO_3} + 3HCl.$$

$$PCl_5 + 4H_2O = \underset{\text{(phosphoric acid)}}{H_3PO_4} + 5HCl.$$

Oxides of phosphorus

There are two important oxides of phosphorus, phosphorus trioxide, P_2O_3, and phosphorus pentoxide, P_2O_5.

Phosphorus trioxide is formed when phosphorus burns in a limited supply of air.

It is a white crystalline solid, and readily oxidizes in the air to form the pentoxide.

Phosphorus pentoxide is formed when phosphorus burns in excess of air.

It is also a white crystalline solid and its most important property is its great affinity for water, with which it combines to form metaphosphoric acid, HPO_3:

$$P_2O_5 + H_2O = 2HPO_3.$$

It is consequently used as a drying agent, and is even more effective than concentrated sulphuric acid.

Like sulphuric acid, it is able to extract the elements of water from many substances. For example, nitric acid loses water to form nitric anhydride (nitrogen pentoxide):

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

That its affinity for water is even greater than that of concentrated sulphuric acid is shown by the fact that it can take the elements of water from sulphuric acid itself, leaving sulphuric anhydride (sulphur trioxide):

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

Acids of phosphorus

There are many acids of phosphorus: phosphorous, orthophosphoric, pyrophosphoric, and metaphosphoric acids.

Orthophosphoric acid, H_3PO_4

This is commonly called phosphoric acid, and is the only acid of phosphorus that we shall consider.

It is formed by the action of phosphorus pentachloride on water, or phosphorus pentoxide on hot water, or by boiling metaphosphoric acid with water.

It is generally prepared, however, by the oxidation of red phosphorus by moderately concentrated nitric acid:

$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O.$$

Properties. — Orthophosphoric acid is a colourless crystalline solid soluble in water. The molecule has three replaceable hydrogen atoms, and so is tribasic; it forms three series of salts:

H_3PO_4	Phosphoric acid.
NaH_2PO_4	Sodium dihydrogen phosphate.
Na_2HPO_4	Disodium hydrogen phosphate. (Ordinary laboratory sodium phosphate.)
Na_3PO_4	Trisodium phosphate.

Tests for phosphoric acid and phosphates. — Solutions of phosphoric acid and phosphates, in the presence of nitric acid, give a yellow precipitate with ammonium molybdate solution.

Silver nitrate solution gives a yellow precipitate of silver orthophosphate, soluble in nitric acid and ammonia.

Matches

The chief use of phosphorus is in the manufacture of matches. Safety-match heads consist of some inflammable

substance, usually antimony sulphide and potassium chlorate. Red phosphorus is used in the surface on which the match is struck. This surface is roughened by the addition of powdered glass, and the friction between the match head and the prepared surface changes the red phosphorus to white phosphorus, which ignites the inflammable mixture on the match head.

For matches that will strike on any rough surface, a sulphide of phosphorus, P_4S_3, is used.

QUESTIONS

1. Describe the manufacture of phosphorus. For what is phosphorus used?

2. Write an account of the properties of white phosphorus and red phosphorus.

3. Describe the laboratory preparation of phosphine. What are "Holmes signals"?

4. How are phosphorus trichloride and phosphorus pentachloride prepared?

5. Give reasons for classifying nitrogen and phosphorus as members of the same "chemical family".

6. Write a paragraph on each of the following: phosphorus trioxide, phosphorus pentoxide, orthophosphoric acid.

7. Silver nitrate solution is found to give a yellow precipitate when added to a solution of a certain sodium salt. What further tests would you apply to find out what salt it is?

CHAPTER XXI

CARBON

Occurrence

Carbon occurs in the free state in large quantities in the earth's crust. Coal consists largely of the element. A purer naturally occurring form of carbon is the crystalline form, graphite, while diamond is the purest form found in nature.

Carbon occurs to a very great extent in the combined state. The chalk and limestone hills of our country consist of calcium carbonate, $CaCO_3$, and this compound of carbon alone occurs in vast quantities in many parts of the earth. Carbon dioxide occurs to a small extent in the atmosphere.

All living organisms contain carbon, and the number of carbon compounds known amounts to hundreds of thousands. So vast is this array of carbon compounds that they are all studied under the separate title of "organic chemistry". Organic chemistry originally meant the study of compounds derived from animal or vegetable organisms, that is, from organic matter. However, as many of these compounds can be made in the laboratory, and derivatives prepared that are not known to occur in nature, almost all carbon compounds are now included in organic chemistry. That is, organic chemistry is the chemistry of carbon compounds. In inorganic chemistry we study a limited number of carbon compounds, such as oxides of carbon and carbonates.

Allotropic forms of carbon

Carbon, like sulphur and phosphorus, exhibits the phenomenon of allotropy, occurring in two crystalline

forms, diamond and graphite. "Amorphous" varieties of carbon consist of extremely minute crystals of graphite.

Diamond. — Diamonds occur in South Africa, Australia, and elsewhere, and consist of colourless octahedral crystals. It is to be noted that the shape of diamonds in jewellery is due to the art of the diamond cutters; the stone is cut in such a way that the maximum lustre is obtained. The natural crystalline shape of diamond is an octahedron (fig. 59).

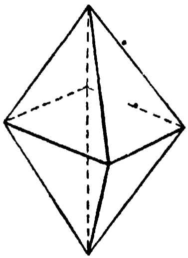


Fig. 59. — Diamond

Diamond has a specific gravity of 3·5, and a very high refractive index (2·417). It is the hardest substance known, and is used for glass cutting and rock boring.

Graphite. — Graphite is a soft dark lustrous substance, crystallizing in hexagonal plates (fig. 60). Its specific gravity is 2·5. It occurs to a small extent in Cumberland, and in large quantities in Ceylon and other countries. Graphite of a high degree of purity is made in large quantities where electricity is cheap, by heating coke, together with a small quantity of sand and pitch, to a very high temperature in an electric furnace.

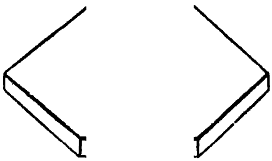


Fig. 60. — Graphite

Graphite, also known as "black lead", is used as a lubricant and for making pencils.

"Amorphous" carbon

Coal, coke, soot, charcoal, and gas carbon are all varieties of what is known as "amorphous" carbon. They are all in reality composed of minute crystals of the stable allotrope, graphite.

Coal. — Coal is a black mineral formed by the decay of vegetable matter under high pressure. It exists in

different forms, according to the conditions under which it was formed.

Anthracite is the purest form of coal, containing over 90 per cent of carbon, very little volatile matter, and very little ash. It is thus a very useful "smokeless" and slow-burning fuel, but of no use in the manufacture of coal gas. **Bituminous coal** is the variety in general domestic use. It contains about 80 per cent of carbon and more volatile matter and a little more ash than anthracite. **Cannel coal** also contains a fairly large proportion of volatile matter, and was formerly used for the manufacture of coal gas; nowadays certain (coking) kinds of bituminous coal are mainly used.

Effect of heat on coal

Place some powdered house coal (not anthracite) in a hard glass combustion tube fitted with delivery tubing leading to a boiling tube kept cool in a beaker of water.

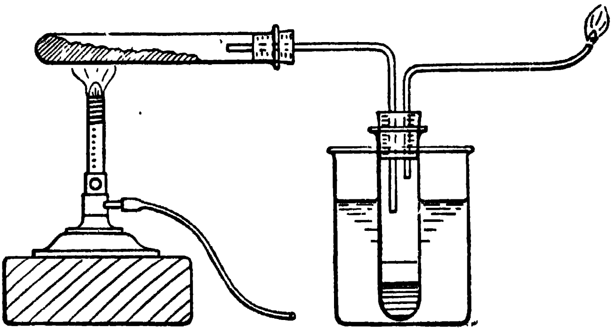


Fig. 61. — To show the Effect of Heat on Coal

A piece of glass tubing in the form of a jet leads from this boiling tube (fig. 61).

On heating the coal for some time it will be seen that there are three main products: coke, left in the combustion tube; liquids — a heavy dark brown oil, coal

tar, and an aqueous liquid above it — condensed in the boiling tube; and gas, which can be burnt at the jet.

Manufacture of coal gas

In a gas works the coal is subjected to heat, when it decomposes as in the experiment above, and the separate products are collected.

The coal is heated in a series of large fireclay retorts heated by a furnace (fig. 62). The volatile products pass from the retorts to the *hydraulic main*, which contains water and some condensed coal tar. The ascension pipe

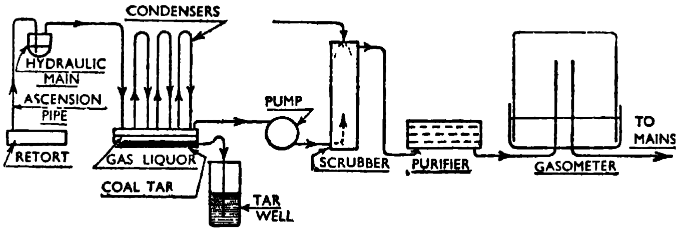


Fig. 62. — Diagram to illustrate the Manufacture of Coal Gas

dips under the surface of the liquid in the hydraulic main to prevent " back lash " when the retort is discharged.

From here the gas is led through a long series of iron pipes, the *condensers*. The liquids condense in two layers, *coal tar* and *gas liquor*, the latter containing ammonia and ammonium salts in solution. The tar is led to the tar well.

The gas is drawn through the condensers by means of an exhaust pump, and passes to the *scrubbers*. These are towers filled with coke down which a spray of water trickles. The water from the *scrubbers* removes more ammonia, and is added to the gas liquor.

The gas still contains sulphur compounds, principally hydrogen sulphide, and these are removed in the purifiers, a series of low rectangular iron tanks fitted with shelves containing *bog iron ore*, $Fe_2O_3{\cdot}H_2O$. This absorbs

the hydrogen sulphide, forming ferric sulphide. When all the oxide has been converted to sulphide it is removed and exposed to the air, which oxidizes it back to the oxide, liberating free sulphur. It is then used again. After it has been used a number of times it contains so much sulphur that its efficiency is impaired, and it is discarded and replaced by fresh bog iron ore. The *spent oxide*, as it is called, is a source of sulphur for the manufacture of sulphuric acid. Its advantage over iron pyrites for this purpose is that it contains no arsenic.

The coal gas is stored in gasometers, and pipes lead from these to the gas mains for general use.

Water gas (p. 220) is generally made at the gas works and mixed with the coal gas. The amount so added depends upon the supply of coal and the demand for coke. The maximum amount is 30 per cent. It is not now "carburetted" (treated with oil while hot to add hydrocarbons which burn with a luminous flame) as formerly.

Coal gas generally consists of hydrogen 50 per cent, methane (a hydrocarbon) 30 per cent, carbon monoxide 8 per cent, hydrocarbons other than methane 5 per cent, together with small quantities of other gases, such as nitrogen, carbon dioxide, and oxygen.

Summarizing, the products of the dry distillation of coal are:

(*a*) coke, the solid residue left in the retorts;
(*b*) gas liquor, from which ammonia is recovered and converted into ammonium sulphate;
(*c*) coal tar, a source of countless valuable chemicals, including drugs, dyes, and explosives;
(*d*) coal gas.

Coke. — Coke is a very useful form of carbon. It burns without smoke and gives out much heat, but requires more draught than coal. It is used for the commercial reduction of metallic oxides to metals, for example, in the smelting of iron.

Lampblack. — This soot is specially made by burning substances rich in carbon in a limited supply of air. It is used for making shoe polish, printer's ink, and black pigments generally.

Gas carbon. — Gas carbon is a hard desposit of greyish-black carbon found on the inner walls of the retorts in a gas works. Its chief use is for making carbon rods for electrical purposes, as it is a good conductor of electricity.

Wood charcoal. — This is made by heating wood or burning it in a limited supply of air. Its chief use

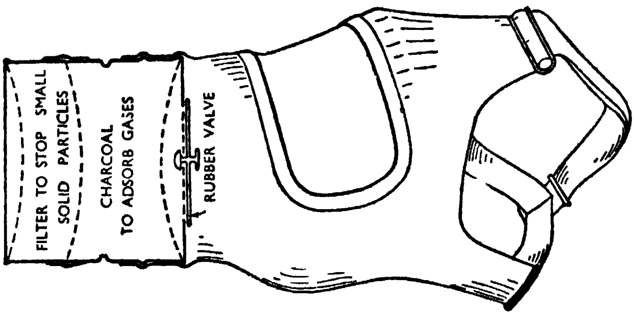


Fig 63 — Diagram of British Civilian Respirator, (original form)

nowadays is as an adsorber of gases. It is porous, and so a small mass of charcoal has a very large surface. Adsorption is the formation of a layer of the gas on a surface, and a porous mass of carbon, such as charcoal, can adsorb large quantities of gas. One volume of coconut charcoal can adsorb as much as 171 volumes of ammonia at S.T.P. Coconut charcoal, specially "activated" by heating, is used in gas masks (fig. 63).

Animal charcoal (bone black) is made by heating bones in closed retorts. It is a good adsorber, having a very large surface, since the carbon is disseminated over a very large area of calcium phosphate Animal

charcoal is very useful in removing colouring matter from many solutions. It is used for removing the brown colour from crude sugar solution, making the familiar white sugar.

Chemical properties of carbon

Carbon burns in air or oxygen, forming carbon dioxide:

$$C + O_2 = CO_2.$$

It also combines directly with sulphur, when sulphur vapour is passed over red-hot coke. Carbon disulphide is formed:

$$C + S_2 = CS_2.$$

One of the most important properties of carbon is that it is a good reducing agent. Many oxides of metals are reduced when heated strongly with carbon. In many cases commercial extraction of the metal is brought about by heating the oxide strongly with coke, e.g.

$ZnO + C = Zn + CO$ (see extraction of zinc, p. 274).
$Fe_2O_3 + 3C = 2Fe + 3CO$ (see extraction of iron, p. 255).

When heated with concentrated sulphuric acid, carbon reduces the acid to sulphur dioxide:

$$C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2.$$

It may be shown that graphite, charcoal, etc., are all forms of carbon, by the fact that each burns in oxygen, forming carbon dioxide only, and that equal weights of each form yield equal weights of carbon dioxide.

The sample of carbon is placed in a porcelain boat in a combustion tube (fig. 64, p. 210). In the tube, beyond the boat, is some granulated copper oxide, kept in place by loose plugs of asbestos. On passing pure dry oxygen over the heated carbon, carbon dioxide is formed. The purpose of the heated copper oxide is to oxidize any carbon monoxide that may have been formed to the

dioxide. The carbon dioxide is absorbed in the weighed potash bulbs, containing potassium hydroxide solution.

The loss in weight of the porcelain boat and its contents gives the weight of carbon used, and the gain in weight of the potash bulbs gives the weight of carbon dioxide formed.

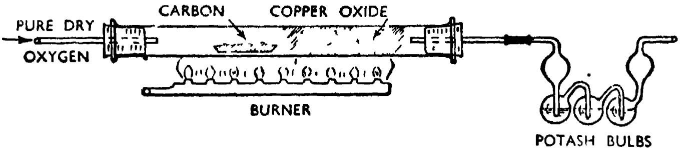


Fig. 64. — Proof that Graphite, Charcoal, etc., are all forms of Carbon

It is found that, no matter what form of carbon is used, 1 gm. of carbon yields 3·67 gm. of carbon dioxide.

OXIDES OF CARBON

Carbon forms two important oxides, carbon monoxide and carbon dioxide, both of which are gases.

Carbon dioxide, CO_2

This gas occurs in the air to the extent of about ·04 per cent of its volume. It is found issuing from the earth in various places, and is in solution in natural mineral waters. It is continuously being formed by the combustion of organic substances such as coal and petrol, and in exhaled breath. Decay of animal and mineral matter also produces carbon dioxide.

The proportion of carbon dioxide in the atmosphere is kept fairly constant because it is absorbed as food by green plants. With the aid of light from the sun and the catalytic effect of **chlorophyll**, the green colouring matter in plants, the carbon dioxide is absorbed, the carbon is retained and changed into starch and sugar, and the oxygen is returned to the atmosphere.

Preparation. — Carbon dioxide is evolved when any acid reacts with any carbonate. It is generally prepared in the laboratory by the action of dilute hydrochloric acid on marble (a form of calcium carbonate):

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The marble chips are placed in a Woulfe bottle (fig. 65) and dilute hydrochloric acid is added by a thistle funnel. The gas is collected by upward displacement of air, or it can be collected over water, in which some will dissolve.

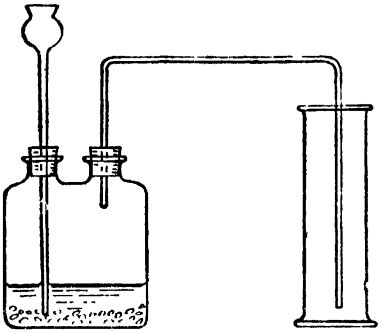


Fig. 65. — Preparation of Carbon Dioxide

Sometimes a Kipp's apparatus (see p. 179) is employed, so that carbon dioxide is " on tap " for use at any time when needed.

It is to be noted that while it is true that carbon dioxide is formed by the action of any carbonate on any acid, lumps of marble and dilute sulphuric acid cannot be employed. This is because calcium sulphate is formed, and this insoluble solid adheres to the lumps of marble and prevents further acid from reaching it.

If a few marble chips are placed in a test-tube and dilute sulphuric acid added, immediate effervescence is observed, but after a few seconds the reaction is seen to slow down, and it soon stops. If the lumps of marble

are removed and scraped with a knife or file and replaced in the acid, further brief effervescence is observed, and this soon stops as before.

Carbon dioxide can also be prepared by heating carbonates, with the exception of sodium carbonate and potassium carbonate.

For example, copper carbonate on heating decomposes to form copper oxide and carbon dioxide:

$$CuCO_3 = CuO + CO_2.$$

The bicarbonates of sodium and potassium give off carbon dioxide when heated. Pure carbon dioxide is often prepared in the laboratory by heating sodium bicarbonate in a hard glass test-tube:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Industrial preparation. — Carbon dioxide is prepared on the large scale by the fermentation of sugars in the manufacture of beer. It is also collected from limekilns during the preparation of quick-lime from limestone or chalk.

Properties. — Carbon dioxide is a heavy colourless gas with a faint sharp smell. It is slightly soluble in water, giving a slightly acid solution; the water dissolves about its own volume of carbon dioxide at ordinary temperature and pressure. The amount dissolved in water is greatly increased by increasing the pressure.

Carbon dioxide will not burn, nor will it support combustion — in fact, the presence of 3 per cent of the gas in air prevents the air from supporting the combustion of most substances, even though oxygen is present to the extent of 18 per cent. The gas will, however, support the combustion of burning magnesium. If a length of magnesium ribbon, held with crucible tongs, is lit in a Bunsen flame and then plunged into a gas jar full of carbon dioxide, it will continue to

burn, spluttering somewhat, and black specks of carbon will be seen in the jar:

$$2Mg + CO_2 = 2MgO + C.$$

The gas is readily soluble in a solution of sodium or potassium hydroxide, with which it reacts to form sodium or potassium carbonate:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

This property is employed to remove carbon dioxide from a mixture of gases, potassium hydroxide being generally used, particularly if we wish to weigh the gas absorbed (see p. 210).

The action of carbon dioxide on lime water is interesting, and it is used as a test for the gas. Lime water is a solution of slaked lime (calcium hydroxide) in water. On first bubbling the gas through the solution a slight turbidity is observed, which increases to a milkiness. Fine white particles of a solid can be seen in the solution; these are particles of calcium carbonate:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

On further passing the gas through the solution, the cloudiness lessens and finally disappears. This is due to the formation of calcium bicarbonate, $Ca(HCO_3)_2$, which is soluble in water:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

On boiling this clear solution it again becomes cloudy, the calcium bicarbonate decomposing. The reaction is the reverse of the previous one:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

Composition of carbon dioxide

A small piece of charcoal is placed in a metal spoon in oxygen over mercury in an apparatus shaped as shown in fig. 66. The carbon is ignited by passing a current of

electricity through the thin piece of platinum wire touching the piece of charcoal. When the latter has burnt and the apparatus has cooled back to room temperature, the volume of gas in the apparatus is found to be unchanged.

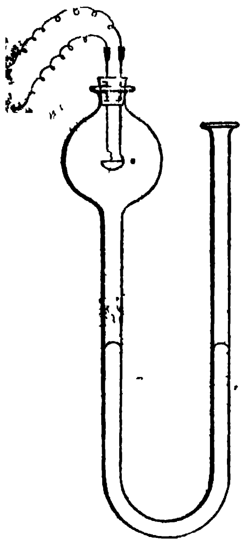


Fig. 66. — Apparatus for determining the Composition of Carbon Dioxide

The carbon has burnt in the oxygen to form carbon dioxide. That is,

1 volume of carbon dioxide contains 1 volume of oxygen;

∴ by Avogadro's hypothesis, 1 molecule of carbon dioxide contains 1 molecule of oxygen. But 1 molecule of oxygen contains 2 atoms, and so 1 molecule of carbon dioxide contains 2 atoms of oxygen.

Now the vapour density of carbon dioxide is found to be 22, and so its molecular weight is 44.

The molecule, however, contains $O_2 = 2 \times 16 = 32$ units of oxygen;

∴ weight of carbon in the molecule $= 44 - 32 = 12$ units of carbon. As 12 is the atomic weight of carbon, the molecule contains 1 atom of carbon.

That is, the formula for carbon dioxide is CO_2.

Uses of carbon dioxide.

We have said that carbon dioxide dissolves in water, the solubility increasing to a great extent when the pressure is increased. This fact is used in the manufacture of soda water, which consists of carbon dioxide dissolved in water under pressure. A solution containing somewhat less carbon dioxide, together with some colouring and

flavouring, constitutes the "mineral water" so beloved of the schoolboy.

Another use of carbon dioxide is in fire extinguishers. In one type a glass phial of sulphuric acid is surrounded by a solution of sodium bicarbonate. On striking the knob at the top of the apparatus, the acid phial is broken, the acid mixes with the carbonate and reacts, and a mixture of sodium sulphate solution and carbon dioxide is ejected.

Carbon dioxide is used medically, being administered with anæsthetics to deepen the breathing of the patient.

Carbon dioxide is also used in refrigerators, in place of ammonia, but is not so efficient.

Solid carbon dioxide is very useful as a freezing mixture, being used to a large extent in keeping ice-cream cool. It is called "carbon dioxide snow" on account of its snowy appearance; and also "dry ice".

Carbonic acid, H_2CO_3

The solution of carbon dioxide in water is, as we have seen, slightly acid. It turns blue litmus paper claret colour. Part of the carbon dioxide in solution has combined with the water, forming **carbonic acid**:

$$H_2O + CO_2 = H_2CO_3.$$

Although carbonic acid itself has not been isolated, its salts, the **carbonates**, are well known. As is seen from the formula, the acid is dibasic, and so gives rise to two series of salts:

H_2CO_3 (carbonic acid).
$NaHCO_3$ (sodium bicarbonate).
Na_2CO_3 (sodium carbonate).

Test for carbonates

All carbonates react with acids, giving off carbon dioxide, and this affords a good test for carbonates. To

the suspected carbonate add dilute hydrochloric acid, and if a gas is evolved bubble it through lime water in a test tube. If the lime water turns cloudy, the gas is carbon dioxide, and so the substance is a carbonate.

Carbon monoxide, CO

Preparation. — This poisonous gas is normally prepared in the laboratory from concentrated sulphuric acid and oxalic acid. The sulphuric acid removes the elements of water from the oxalic acid, and a mixture of carbon monoxide and carbon dioxide is evolved.

$$\underset{\text{(oxalic acid)}}{H_2C_2O_4} - \underset{\text{(removed by } H_2SO_4)}{H_2O} = CO_2 + CO.$$

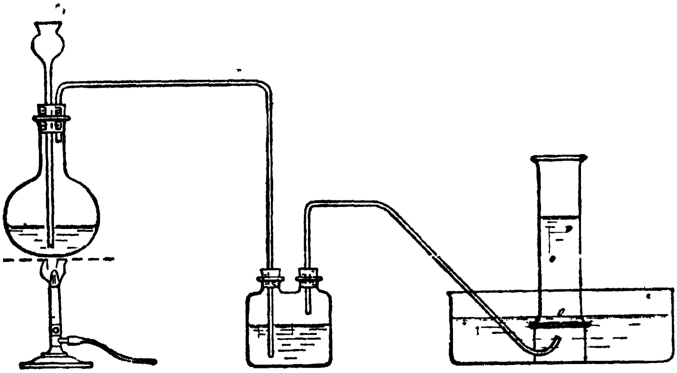


Fig 67 — Preparation of Carbon Monoxide from Oxalic Acid

Crystals of oxalic acid are placed in a flask fitted with a thistle funnel and delivery tube joined to potash bulbs or a bottle containing potassium or sodium hydroxide solution. From the bottle the delivery tube leads to a gas jar inverted over water (fig. 67).

Concentrated sulphuric acid is poured down the thistle funnel and the flask is gently heated. Carbon dioxide and carbon monoxide are evolved, and the dioxide is

absorbed in the potassium hydroxide or sodium hydroxide solution:

$$CO_2 + 2NaOH = Na_2CO_3 + H_2O.$$
$$CO_2 + 2KOH = K_2CO_3 + H_2O.$$

The carbon monoxide is insoluble in the alkali, and so passes on and is collected in the gas jar.

Another interesting laboratory preparation is reduction of carbon dioxide with carbon:

$$CO_2 + C = 2CO.$$

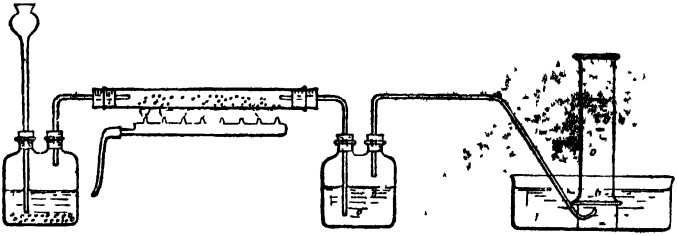


Fig. 68. — Preparation of Carbon Monoxide by reduction of Carbon Dioxide

Carbon dioxide is prepared from marble chips and dilute hydrochloric acid, and the gas is passed through a long copper or silica tube packed with red-hot charcoal. Any unreduced carbon dioxide is absorbed in a bottle of sodium hydroxide solution, and the monoxide passes on, to be collected over water (fig. 68).

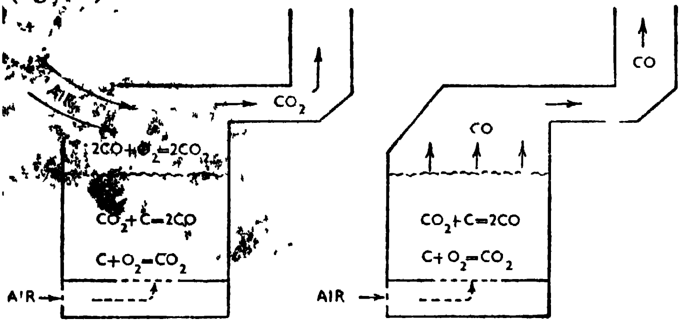
Properties. — Carbon monoxide is a colourless, odourless gas insoluble in water. It burns with a lambent blue flame, forming carbon dioxide:

$$C + O_2 = CO_2.$$

It does not support combustion and does not react with lime water. The gas is very poisonous and is particularly dangerous on account of its having no smell. Its poisonous action is due to the fact that it reacts with

the hæmoglobin of the blood, forming carboxyhæmoglobin. This prevents the hæmoglobin performing its proper function of absorbing oxygen to form oxyhæmoglobin. Very small quantities of carbon monoxide are sufficient to cause death. Carbon monoxide is present in the exhaust fumes of petrol engines, and so it is dangerous to run the engine of a car in a garage with the doors closed.

Carbon monoxide is formed in a coal or coke fire (fig. 69).



Open Closed

Fig. 69. — Anthracite Stove

In a coke or anthracite stove, or in a coal fire when the volatile matter has burnt and the coals are glowing, the combustion of carbon is as follows:

(*a*) Air enters from below and the carbon burns completely, forming carbon dioxide:

$$C + O_2 = CO_2.$$

(*b*) This carbon dioxide, rising through the red-hot carbon, is reduced to carbon monoxide:

$$CO_2 + C = 2CO.$$

(*c*) If the fire is open, i.e. if more oxygen can get in at the top, the carbon monoxide burns with a pinkish-blue

flame, forming carbon dioxide, which goes up the chimney:

$$2CO + O_2 = 2CO_2.$$

If the fire is closed, as in a slow-combustion stove, oxygen is admitted at the top, and so the carbon monoxide cannot burn but goes up the chimney. In this case it is important not to have any cracks in the top of the stove through which carbon monoxide can escape. It is equally important to see that the flue pipe does not lead loosely into the chimney stack, so that a down draught would blow the poisonous gas into the room. The pipe should either lead directly outside or be cemented into the chimney stack.

Sometimes, on opening this type of stove, the air suddenly coming into contact with the hot carbon monoxide causes a great tongue of pinkish-blue flame of burning gas to be thrown out.

Use. — Carbon monoxide is chiefly used as a fuel in the form of producer gas or water gas.

Producer gas and water gas

It is convenient to make these two fuels together. They are prepared at most gas works, the gases being used to help in heating the retorts. Some of the water gas is mixed with the coal gas.

Producer gas is made by blowing air through a large cylinder of red-hot coke. The coke burns fiercely in the blast of air, forming carbon dioxide. This is reduced as it passes up through the red-hot coke, forming carbon monoxide. The reactions are the same as those occurring in a closed anthracite stove, just described. As the air contains nitrogen, producer gas consists of a mixture of nitrogen and carbon monoxide.

Producer gas is widely used in industry, both as a source of heat and for driving gas engines. It is sometimes used in motor vehicles as a substitute for petrol when the latter is scarce, as in war time.

Water gas. — After air has been passed through the coke for some minutes in the preparation of producer gas, the coke gets white-hot, since great heat is given out. The air blast is then shut off and steam is passed through. This is reduced by the carbon, forming hydrogen and carbon monoxide:

$$H_2O + C = H_2 + CO.$$

Heat is absorbed in this reaction, and so the temperature of the coke falls. When the coke is only red-hot, the steam is shut off and air is again blown in. Thus producer gas and water gas are produced alternately.

QUESTIONS

1. Write an account of the allotropic forms of carbon. How would you show that graphite and lampblack are forms of the same element?

2. Describe the manufacture of coal gas.

3. Describe two experiments to show that carbon is a reducing agent.

4. What are the chief uses of the different forms of carbon?

5. How is carbon dioxide prepared in the laboratory?

6. What are the chief properties and uses of carbon dioxide?

7. Describe an experiment to show that carbon dioxide contains its own volume of oxygen. Give reasons for assuming that the formula for carbon dioxide is CO_2.

8. Describe a laboratory method for the preparation of carbon monoxide. What are its principal properties?

9. Describe the chemical changes that occur when anthracite burns in a stove.

10. Describe the manufacture of producer gas and water gas. What are their chief uses?

11. What volume of carbon dioxide at S.T.P. can be prepared from 20 gm. of marble?

CHAPTER XXII

SILICON

Occurrence

Next to oxygen, silicon is the most abundantly occurring element in the earth's crust although it is not found uncombined. It occurs chiefly as the oxide, silica, and as silicates. The silicates may be considered to be compounds of silica and basic oxides.

Sand, quartz, and flint consist of silica. Many rocks, such as basalt and granite, and also clay, consist largely of silicates.

Preparation

The element (Si) may be prepared by heating silica with magnesium:

$$SiO_2 + 2Mg = 2MgO + Si.$$

So prepared, the element is a brownish amorphous powder. It also exists in crystalline form as a hard greyish solid.

When heated strongly in air it forms silica:

$$Si + O_2 = SiO_2.$$

It burns in chlorine, forming silicon tetrachloride, $SiCl_4$, a volatile liquid.

Silicon, although a non-metal (its oxide is acidic), forms alloys with certain metals. Silicon steel is used in making the cores of electromagnets.

Silica, SiO_2, occurs in crystalline form as **quartz**,

some quartz crystals being very large and well-defined (fig. 70).

Sand consists of small grains of quartz mixed with iron oxide.

Silica is an acidic oxide, since it combines with bases to form salts, known as **silicates.**

When silica is heated very strongly it fuses, and may then be worked like glass. This *quartz glass* is an amorphous form of silica and is very useful for making

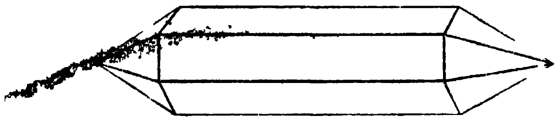


Fig 70. — Quartz Crystal

apparatus, as it has an extremely low coefficient of expansion, and may be heated and cooled rapidly without cracking.

Silicates.

As we have said, silica combines with bases to form silicates. For example, silica dissolves in caustic soda, forming sodium silicate.

$$SiO_2 + 2NaOH = \underset{\text{(sodium silicate)}}{Na_2SiO_3} + H_2O.$$

Sodium silicate, known as *water glass*, is soluble in water and is used for preserving eggs. The calcium silicate formed closes up the pores of the egg-shell and prevents air getting in.

Glass consists of a mixture of silicates. When a mixture of sodium carbonate and calcium carbonate is fused with silica, a mixture of sodium silicate and calcium silicate is formed:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$
$$SiO_2 + CaCO_3 = CaSiO_3 + CO_2.$$

This mixture is ordinary *soft glass*, and is used for making bottles, test tubes, flasks, etc.

Hard glass. — This fuses at a higher temperature than ordinary soft glass It is made from potassium carbonate instead of sodium carbonate, and [illegible] consists of a mixture of potassium and calcium silicates.

Flint glass, used for making lenses and prisms on account of its high refractive index, consists of potassium silicate and lead silicate. It is softer than ordinary glass, and care must be taken not to scratch lenses when polishing them.

Coloured glass is made by the addition of various metallic oxides to ordinary glass.

Glass is really a supercooled liquid, that is, a liquid cooled below its freezing-point without the particles forming themselves into a crystalline structure. If glass is heated it will not, as a true solid should, melt a a definite temperature; it gradually gets softer and softer over a very wide range of temperature. Glass very slowly crystallizes, and when this has occurred it is very brittle and is of no use. The glass is then said to be *devitrified*.

Silicon carbide, SiC

Silicon carbide, known as **carborundum**, [illegible] is made by heating a mixture of silica and coke [illegible] temperature in an electric furnace:

$$SiO_2 + 3C = SiC + 2CO$$

Carborundum is very hard, and so [illegible] abrasive for sharpening tools, grinding [illegible] valves of engines, etc.

QUESTIONS

1. What are the chief properties of silicon?

2. How does silica occur in nature? What happens when silica is heated very strongly?

3. Write a paragraph on each of the following: water glass, soft glass, hard glass, flint glass, carborundum.

CHAPTER XXIII

METALS AND NON-METALS

Most people can tell at a glance whether a certain substance is a metal or not. Their judgment is no doubt based on the peculiar lustre which metals possess.

It is to be noted, however, that in chemistry we do not refer to all substances which are not metals as "non-metals". It is wrong, for instance, to call glass and wood non-metals, even though they are not metallic in ap-arance or other properties; they consist of compounds, ' are made up of metals and non-metals. A non-metal *element* that is not a metal. Thus, sulphur, nitrogen, , phosphorus, and bromine are all non-metals.

s compare the properties of metals and non-als (see table opposite). Exceptions to the rule are put brackets.

The most important difference between metals and metals is that metals form basic oxides while non-form acidic oxides. If there is any doubt whether lent is a metal or a non-metal, that is the decisive it forms a basic oxide, it is a metal. Some metals n acidic oxides as well as basic, but the normal oxide basic. No non-metal forms a basic oxide.

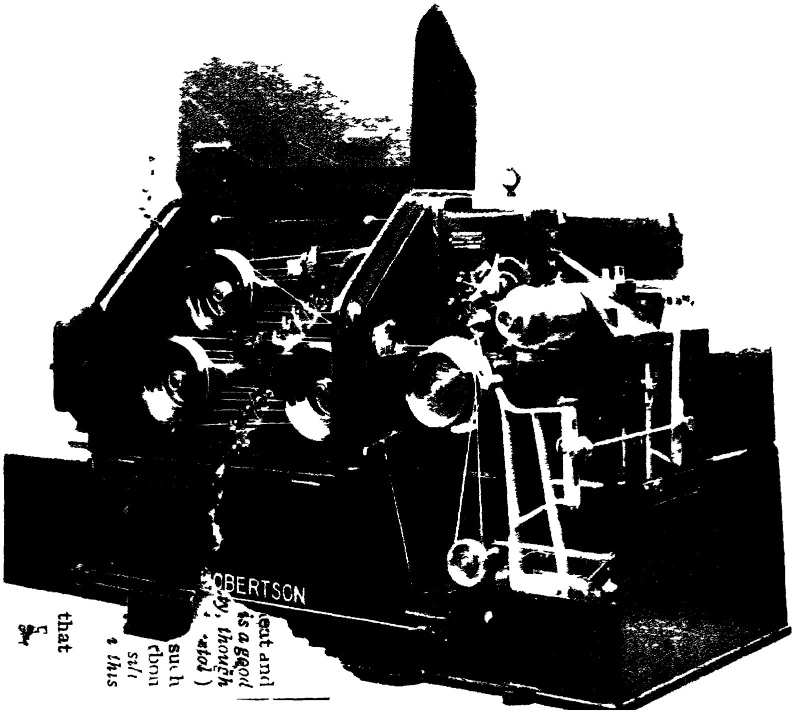
Alloys

Most metals when melted with another metal mix with it to form a homogeneous liquid. On cooling, an intimate mixture is formed. This is called an **alloy.**

Generally these solid mixtures are not homogeneous: on examination under the microscope separate crystals are observed.

WIRE DRAWING MACHINE

This illustrates the ductility of metals. The machine draws copper wire from .104 inch diameter to .0108 inch diameter, each of the 21 diamond dies reducing the wire by [illegible] cross sectional area. One yard of .104 inch wire lengthens to 93 yards of .0108 inch wire which is wound on the spool at the top right of the photograph.



METALS	NON-METALS
Physical Differences	
Exhibit a peculiar lustre on their surface; they can be polished and reflect light regularly.	Have no such lustrous appearance. (*Graphite and iodine, however, show some sort of metallic-looking sheen.*)
Are all solids at ordinary temperatures. (*Mercury is liquid.*)	Some are solids, some liquids, and some gases.
Have high melting-points and very high boiling-points. (*Mercury has a melting-point below 0° C. and sodium and potassium below 100° C.*)	Have low melting-points and boiling-points. (*Carbon and silicon have very high melting-points.*)
Have high specific gravities. (*Sodium and potassium have a specific gravity less than 1.*)	Have low specific gravities. (*Iodine has a specific gravity of 4·9.*)
Are malleable and ductile. That is, they can be hammered into sheets and drawn into wire. (*Zinc is rather brittle.*)	If solids, are brittle. (*Plastic sulphur is not brittle.*)
Are good conductors of heat and electricity.	Are bad conductors of heat and electricity. (*Graphite is a good conductor of electricity, though not as good as th[illegible] metal.*)
Do not dissolve, except in other metals.	Dissolve in some solvent, such as water, alcohol, or carbon disulphide. (*Carbon and silicon behave like metals in this respect.*)
Are electropositive, that is, they go to the cathode in electrolysis.	Are electronegative, that [illegible] they go to the an[illegible] trolysis.
Chemical Differences	
Form basic oxides.	Form acidic oxides.
Chlorides are true salts and are not decomposed by water.	Chlorides are not true salts, and are decomposed by water.
Either do not form compounds with hydrogen, or form non-volatile, unstable compounds.	Form stable volatile compounds with hydrogen.
Do not react with one another to form stable compounds, but react with non-metals.	React with both metals and non-metals.

Some important alloys are given in the table below:

Alloy	Composition	Advantages	Use
Brass.	Copper and zinc.	Easily turned, cast, and soldered.	Machine parts, ornaments
Bronze.	Copper and tin.	Strong.	Coinage, machine parts, statuary
Solder.	Lead and tin.	Low melting-point	Soldering
Stainless steel.	Iron, carbon, and chromium.	Does not rust or tarnish	Cutlery.
Cobalt steel.	Iron, carbon, and cobalt	Retains magnetism well.	Permanent magnets.

THE ELECTROCHEMICAL SERIES

It is known that if zinc and copper plates are dipped into a dilute acid and are connected externally by an electrical conductor, a current of electricity flows in the conductor from the copper to the zinc. Within the electrolyte the current flows from the zinc to the copper. When in the acid, the copper is said to be at a higher potential than the zinc.

Other pairs of metals can be used, and a list can be compiled in which, if any two are placed in an electrolyte, the external current will flow from the metal in the lower position to that in the higher position. In the electrolyte the current flows from the metal in the higher position to that in the lower. Thus our list will consist of the metals in order of their potentials when in contact with an electrolyte, and it is called the **electrochemical series.**

The following is the series, so far as the metals which we are studying meanwhile are concerned:

Potassium.	Aluminium.	Copper.
Sodium.	Zinc.	Mercury.
Calcium.	Iron.	Silver.
Magnesium	Lead.	

Thus, if plates of silver and iron are placed in dilute sulphuric acid and connected up to make a cell, the current in the external circuit would be from the silver to the iron, and in the acid the current would flow from the iron to the silver.

This list of metals does not merely concern electrical potential; if that were the case, this book would be no place to discuss it. It is found, however, that there is a gradation in the *chemical properties* of metals as we proceed down the list.

You know, doubtless, that if a penknife blade is dipped into a solution of copper sulphate it becomes coated with copper. Actually there is an exchange of metals: iron dissolves from your knife blade, forming ferrous sulphate, and copper is liberated as metal and adheres to the blade:

$$Fe + CuSO_4 = FeSO_4 + Cu.$$

It is found that when a metal displaces another metal from a solution of its salts, it is higher in the electrochemical series than the metal it displaces. Thus zinc will displace copper and silver from solutions of copper sulphate and silver nitrate respectively.

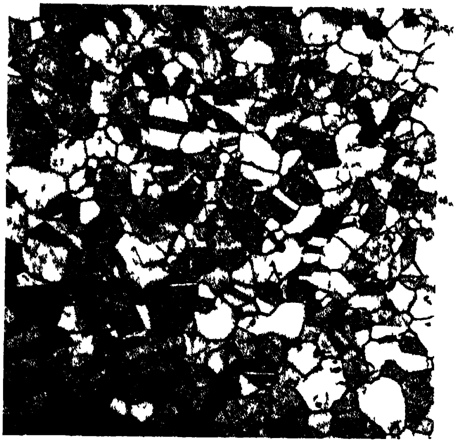
The electrochemical series is also the order of chemical activity and stability of metals. For example, potassium and sodium are extremely active, as is seen by their action with water, and in their other properties. The metals are consequently not found in the free state and are difficult to isolate. Metals low in the list are found in the free state (gold has a position below that of silver) and are easily isolated from their compounds. The metals down the list as far as iron liberate hydrogen from dilute sulphuric and hydrochloric acids, with decreasing readiness, and from lead downwards they do not do so. Similarly, the metals down as far as calcium liberate hydrogen from cold water, with decreasing readiness, and the heated metal does so from steam down as far as iron. Below iron on the list they do not decompose water.

In compounds of metals, too, there is this gradation of properties. For example, the oxides of metals down the list as far as copper are stable when heated, but below they decompose, liberating oxygen and leaving the metal. The oxides down as far as zinc are not reduced when hydrogen is passed over the heated metal, but from iron down the list they are reduced to the metal, water being formed.

Some cases of this gradation in properties of metals and their compounds down the electrochemical series are shown in the following table:

K	Na	Ca	Mg	Al	Zn	Fe	Pb	Cu	Hg	Ag
Decompose cold water, giving hydroxide and hydrogen.			Heated metal decomposes steam, giving oxide and hydrogen.				Stable to water and steam.			
Readily oxidized; burn in air or oxygen.							Oxidize when heated in air.			Not oxidized.
Displace hydrogen from dilute hydrochloric or sulphuric acid.							Not attacked by dilute hydrochloric or sulphuric acid.			
Oxides stable when heated.									Oxides decompose on heating.	
Form soluble hydroxides.			Form insoluble hydroxides.						Form no hydroxides.	
Nitrates decompose on heating to give nitrites.		Nitrates decompose on heating to give oxides.							Nitrates decompose on heating to give metals.	

MILD STEEL HOT ROLLED AND ANNEALED (× 100)



F 18

MONEL METAL (NICKEL AND COPPER) (× 100)

QUESTIONS

1. Write down the principal physical and chemical differences between metals and non-metals

2. Give examples to show how the physical properties of metals are utilized.

3. Give as many reasons as you can for assuming copper to be a metal, and sulphur to be a non-metal.

4. What is an alloy? Describe three alloys with which you are familiar, stating their advantages and uses.

5. What is the *electrochemical series*? What is its importance in chemistry?

CHAPTER XXIV

SODIUM AND POTASSIUM

SODIUM

Occurrence

Sodium does not occur in nature in the free state. This is to be expected, since it is an extremely active substance. Sodium salts, however, occur widely in the earth's crust. Sodium chloride is the principal solid in solution in sea water, and sodium nitrate occurs in the vast caliche deposits of Chile.

Sir Humphry Davy isolated sodium in 1807 by the electrolysis of fused sodium hydroxide. The principle of his method is used in the preparation of sodium to-day.

Industrial preparation.

The sodium hydroxide is made from common salt by electrolysis. The caustic soda is fused in an iron pot, with a cylindrical iron rod as cathode. A nickel cylinder serves as anode and is separated from the cathode by a wire gauze cylinder (fig. 71).

The caustic soda decomposes on electrolysis:

$$NaOH = Na^+ + OH^-.$$

The sodium is liberated at the cathode and the hydroxyl (OH^-) group cannot exist as such and decomposes at the anode, forming water and liberating oxygen:

$$2OH^- = H_2O + O^{--}.$$

The water formed is absorbed by the caustic soda and

is immediately attacked by some of the sodium at the cathode:

$$2Na + 2H_2O = 2NaOH + H_2.$$

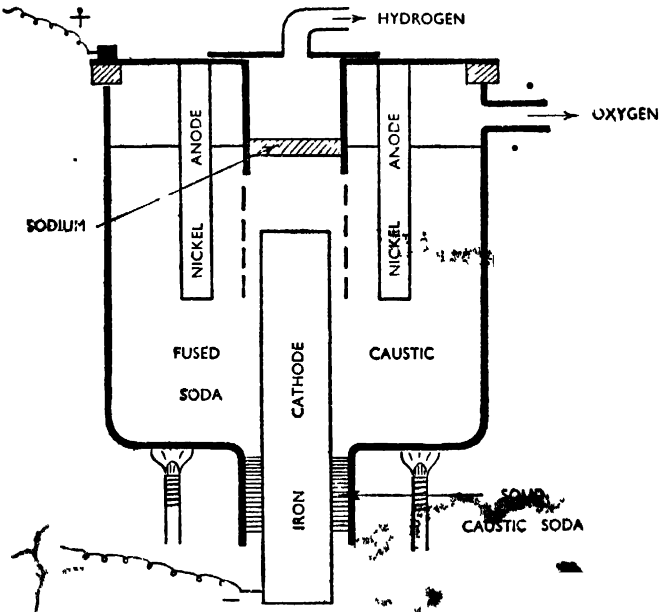


Fig. 71. — Preparation of Sodium

Thus the results of the electrolysis are: sodium and hydrogen are liberated at the cathode, and oxygen is liberated at the anode.

Properties

Sodium is a soft metal with a specific gravity of 0·97. It melts at 97° C. When it is cut with a knife it shows a lustrous silvery surface which very quickly tarnishes, forming sodium oxide, Na_2O:

$$4Na + O_2 = 2Na_2O.$$

The oxide immediately combines with water vapour from the air, forming sodium hydroxide:

$$Na_2O + H_2O = 2NaOH.$$

The sodium hydroxide slowly reacts with carbon dioxide in the air, forming sodium carbonate:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

For this reason, sodium is kept sealed up in tin cans. In the laboratory it is kept in bottles under petroleum.

When heated in the air, sodium melts and burns with a bright yellow flame, forming sodium peroxide:

$$2Na + O_2 = Na_2O_2.$$

Action of sodium on water

When a small piece of sodium is dropped on to the surface of some water in a trough (note: a large portion of sodium with a small amount of water is dangerous), it is noticed that the sodium floats, forms a globule and darts about the surface, diminishing in size until it finally disappears. Hydrogen is given off, which may be burnt if a light is applied. The hydrogen can be collected by wrapping up small pieces of sodium in wire gauze (an old discarded square of wire gauze can be torn up into 16 pieces for the purpose) and dropping them into water. The packages sink, and bubbles of gas rise and can be collected in a test-tube and shown to be hydrogen.

The liquid in the trough is slimy to the touch and alkaline to litmus. It is a solution of sodium hydroxide:

$$2Na + 2H_2O = 2NaOH + H_2.$$

Flame test

When sodium or any compound of sodium is placed in a Bunsen flame, a bright yellow coloration is observed. This colour cannot be seen through blue glass. The flame test is usually performed by heating a piece

F 95

(Photograph by courtesy of I. C. I. (Salt) Ltd.)

EVAPORATION OF INDUSTRIAL BROAD SALT

of platinum wire in a Bunsen flame until there is no coloration of the flame, dipping the wire into dilute hydrochloric acid, and then touching the substance to be tested with the tip of the wet platinum wire. A little adheres, and this is held in the edge of the flame.

Sodium hydroxide, caustic soda, NaOH.

Laboratory preparation. — Sodium hydroxide solution can be prepared in the laboratory by the action of sodium on water, as described above.

It can also be prepared by boiling a solution of sodium carbonate with excess of slaked lime (calcium hydroxide):

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

The lime is added a little at a time to a hot 10 per cent solution of sodium carbonate, stirring while the addition is made. A white solid is seen at the bottom of the beaker, and this consists of calcium carbonate and excess lime. On filtering, a solution of sodium hydroxide is obtained, which may be evaporated if the solid is required.

Industrial preparation

Caustic soda is prepared on the large scale, together with chlorine and hydrogen, by the electrolysis of brine. There are many adaptations of this method, one of the most important being the Castner Kellner process.

When a current of electricity is passed through [illegible] it decomposes into sodium and chlorine. The [illegible] immediately reacts with the water, giving off [illegible] and forming sodium hydroxide. The sodium [illegible] however, reacts with the chlorine, giving sodiu[illegible] and sodium hypochlorite:

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O$$

It is necessary, therefore, if sodium hydroxide is required, to separate the products to prevent them from

reacting. The Castner Kellner cell (fig. 72) is an ingenious arrangement for doing this.

Each cell is divided into three parts by partitions which reach nearly to the bottom of the cell. The two outer compartments contain brine, and the middle one water. Mercury on the floor of the cell separates the compartments, yet connects them electrically.

The anodes, dipping into the brine compartments, are made of carbon, while the cathode in the water of the central compartment is made of iron.

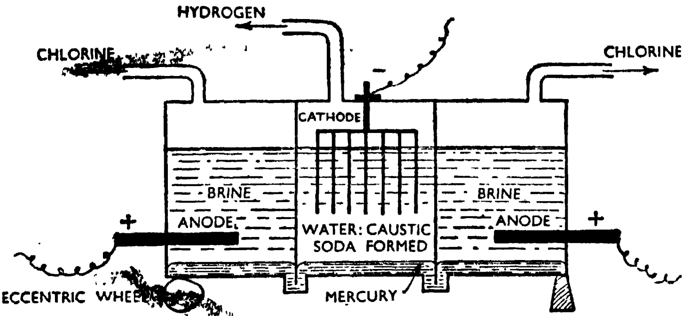


Fig. 72.—Manufacture of Caustic Soda, Chlorine, and Hydrogen. Castner-Kellner Process

Chlorine is liberated at the anodes, and is led off by the pipes as shown. In the two outer compartments the mercury acts as the cathode, and the sodium liberated there immediately forms an amalgam with the mercury. As the cell is rocked by the rotation of the eccentric wheel, the sodium amalgam passes into the central compartment. Here the sodium reacts with the water, forming sodium hydroxide and liberating hydrogen, which escapes by the pipe.

The sodium hydroxide solution is evaporated in iron pans.

Properties

Sodium hydroxide is a very deliquescent white crystalline solid. It is kept, generally in the form of sticks, in airtight bottles, as it reacts with carbon dioxide in the air to form sodium carbonate:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

The solution is very strongly alkaline, turning red litmus blue, and forming sodium salts with acids.

On adding sodium hydroxide to a solution of a salt, the hydroxide is formed. Most of these are insoluble, and so are precipitated. For example, ferric hydroxide, $Fe(OH)_3$, is precipitated as a reddish-brown gelatinous precipitate when sodium hydroxide is added to ferric chloride solution:

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$

Uses of sodium hydroxide

In the laboratory sodium hydroxide is used for absorbing carbon dioxide and sulphur dioxide, and for other purposes.

Commercially it is used for making hard soap, and in the manufacture of glass, artificial silk, and paper.

Sodium chloride, common salt, NaCl

Sodium chloride is a white crystalline solid, occurring in sea water, and underground in solid form as rock salt. It crystallizes in cubes, with no water of hydration.

The deliquescence of common salt is due to the presence of a little calcium chloride as impurity; pure sodium chloride is not deliquescent. Table salt often contains a little sodium bicarbonate, which reacts with the calcium chloride, and so prevents deliquescence.

$$CaCl_2 + 2NaHCO_3 = CaCO_3 + 2NaCl + H_2O + CO_2.$$

Sodium carbonate, Na_2CO_3

Anhydrous sodium carbonate is a white powder. It crystallizes with water of hydration to form large colourless crystals of **washing soda**, $Na_2CO_3 \cdot 10H_2O$.

Industrial preparation

Sodium carbonate is prepared on the large scale by the **Solvay process**, also known as the **ammonia-soda process**.

Brine, nearly saturated with ammonia, enters the top of a tower, down which it trickles slowly (fig. 73). Carbon

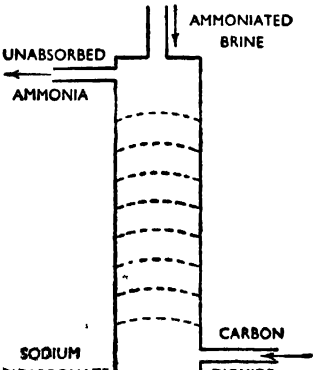


Fig. 73. — Solvay Tower Ammonia-Soda Process

dioxide is passed up the tower under pressure, and reacts with the ammonia, forming ammonium bicarbonate:

$$NH_3 + H_2O + CO_2 = NH_4HCO_3. \qquad \text{(i)}$$

The ammonium bicarbonate thus formed reacts with the sodium chloride, forming ammonium chloride and sodium bicarbonate:

$$NH_4HCO_3 + NaCl = NH_4Cl + NaHCO_3. \quad \text{(ii)}$$

The sodium bicarbonate collects as a white sludge at the bottom of the tower and is pumped out through vacuum filters.

The sodium bicarbonate is heated, when sodium carbonate, a white powder known as **soda ash**, is formed:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2. \quad \text{(iii)}$$

This is dissolved in hot water and crystallized out in the familiar large crystals of soda, $Na_2CO_3 \cdot 10H_2O$.

The ammonia-soda process eliminates waste products in a most ingenious way. The carbon dioxide passed up the tower is made by heating limestone:

$$CaCO_3 = CaO + CO_2. \quad \text{(iv)}$$

The carbon dioxide from equation (iii) is added to the gas produced from the limestone.

Ammonia is recovered from the ammonium chloride formed as shown in equation (ii) by treatment with lime from equation (iv).

$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3.$$

It is seen that theoretically all the amm[illegible] used is recovered Some ammonia escapes at the [illegible] of the tower, but is recovered and absorbed by the [illegible]. In practice the loss of ammonia is very small, but [illegible], of course, to be made up. Calcium chloride is [illegible] waste product in the ammonia-soda process.

Properties

Sodium carbonate forms large crystals of the composition $Na_2CO_3 \cdot 10H_2O$. These effloresce in the air forming the lower hydrate, $Na_2CO_3 \cdot H_2O$, which appears as a white powder covering the clear crystals.

Sodium carbonate does not give off carbon dioxide on heating. Most other carbonates, except potassium carbonate, do so.

Soda is used in households for softening water and [illegible]

cleaning. It is used in the manufacture of glass, water glass, and borax, as well as in other industries.

Sodium bicarbonate, $NaHCO_3$

Sodium bicarbonate can be prepared in the laboratory by passing excess of carbon dioxide into sodium hydroxide solution. At first the carbonate is formed:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

On continuing to pass carbon dioxide, the bicarbonate is formed:

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

It is to be noticed that the above reactions bear a close resemblance to those occurring when carbon dioxide is passed through lime water (calcium hydroxide). In that case, however, the calcium carbonate first formed, being insoluble, is precipitated, the liquid subsequently clearing as more carbon dioxide is passed in and the soluble bicarbonate formed. In the case we are considering, however, both sodium carbonate and sodium bicarbonate are soluble in water, and so no change from one to the other is evident.

It will also be remembered that on boiling the clear solution of calcium bicarbonate, cloudiness is again observed, due to the decomposition of the bicarbonate into the carbonate and carbon dioxide. Similarly, on boiling a solution of sodium bicarbonate, or heating the solid, it decomposes, giving off carbon dioxide and leaving the carbonate:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Pure anhydrous sodium carbonate is generally prepared in the laboratory by heating sodium bicarbonate. This process is also used when carbon dioxide purer than that obtained from marble and dilute hydrochloric acid is required.

Sodium bicarbonate is a white crystalline solid soluble in water. It is used as baking powder, because on heating carbon dioxide is given off, and this aerates the cakes, etc.

Sodium nitrate, $NaNO_3$

This salt occurs in vast quantities in Chile and is known as **Chile saltpetre.**

It is a white crystalline solid soluble in water, the crystals being deliquescent.

On heating sodium nitrate strongly it decomposes, sodium nitrite being formed and oxygen evolved:

$$2NaNO_3 = 2NaNO_2 + O_2.$$

(Other nitrates, with the exception of potassium nitrate, do not behave in this way, but generally decompose on heating, forming the oxide.)

Sodium nitrate is used as a fertilizer and for the manufacture of nitric acid and nitrates.

POTASSIUM

Potassium is an element bearing a very striking resemblance to sodium, both in its own properties and in those of its compounds. Just as chlorine, bromine, and iodine are classed together as a " chemical family " called the halogens, so potassium and sodium, together with some other metals, are classed together. This family of elements is called the **alkali metals.**

Occurrence

Potassium occurs in combination in vast quantities in the Stassfurt deposits, where various potassium salts are found. The chief one is **carnallite**, a double chloride of potassium and magnesium, $KCl{\cdot}MgCl_2{\cdot}6H_2O$.

Potassium is prepared by the same method as that used for the preparation of sodium, namely, the electrolysis of the fused hydroxide.

Properties

Potassium is a soft metal which has a bright lustre when it is freshly cut, but it very quickly tarnishes, forming the oxide, hydroxide, and finally the carbonate, just like sodium It has a lower melting-point than sodium, namely, 62° C., and like sodium it has a specific gravity less than 1, namely, 0·86.

When a small piece of potassium is dropped on to the surface of water, the reaction is similar to that seen with sodium, but is even more vigorous. The heat of the reaction is sufficient to ignite the hydrogen, which is seen to burn with a pale violet flame:

$$2K + 2H_2O = 2KOH + H_2.$$

Flame test

This violet coloration of a flame affords a good test for potassium compounds. All potassium compounds colour a Bunsen flame a pale violet, but the colour is often masked by the strong yellow of sodium compounds, even when only traces of the latter are present. It will be remembered that the yellow sodium coloration is not visible through blue glass. The potassium flame, however, can be seen through it, and so when testing for potassium the flame is always viewed through a piece of blue glass.

Potassium chloride is similar to sodium chloride, crystallizing in cubes without water of hydration.

Potassium hydroxide is prepared by a method similar to that employed for sodium hydroxide, and it has similar properties. It is often used instead of sodium hydroxide for absorbing carbon dioxide and sulphur dioxide.

Potassium carbonate, like sodium carbonate, does not give off carbon dioxide on heating, but **potassium bicarbonate,** like sodium bicarbonate, decomposes on

heating, giving off carbon dioxide and leaving the normal carbonate.

Potassium nitrate (saltpetre), KNO_3, is made from sodium nitrate by treatment with a hot concentrated solution of potassium chloride:

$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl.$$

The above reaction is reversible, but with the concentration used, the sparingly soluble sodium chloride crystallizes out, and the reaction proceeds from left to right in the equation. A solution of potassium nitrate results, from which the nitrate is crystallized on cooling.

Potassium nitrate forms white crystals similar to sodium nitrate, but, unlike the sodium salt, it is not deliquescent. It can therefore be used in the manufacture of gunpowder, since it keeps dry.

Like sodium nitrate, and unlike other nitrates, potassium nitrate decomposes into the nitrite and oxygen on heating:

$$2KNO_3 = 2KNO_2 + O_2.$$

Potassium chlorate, $KClO_3$

It will be remembered that when chlorine is passed into a hot concentrated solution of sodium hydroxide, sodium chlorate is formed (p. 159). (Chlorine and the cold dilute hydroxide give the hypochlorite.) A similar reaction occurs with hot concentrated potassium hydroxide, potassium chlorate being formed. Potassium chlorate is made on the large scale by this method, which is performed as follows.

A hot concentrated solution of potassium chloride is subjected to electrolysis:

$$2KCl = 2K + Cl_2.$$

The potassium formed immediately reacts with the water, forming potassium hydroxide:

$$2K + 2H_2O = 2KOH + H_2.$$

The chlorine formed reacts with the hot concentrated potassium hydroxide solution, forming potassium chlorate:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Potassium chlorate is used in the manufacture of matches, and for the laboratory preparation of oxygen.

QUESTIONS

1. Describe the preparation of sodium.

2. What are the principal properties of sodium?

3. How is sodium hydroxide prepared on the large scale?

4. What are the chief properties and uses of sodium hydroxide?

5. Describe the Solvay process for the manufacture of sodium carbonate. This process is said to be an ideal example of chemical economy. How is this statement justified?

6. Give reasons for classing sodium and potassium together as members of the same "chemical family".

7. Given two white crystalline substances said to be sodium and potassium chlorides, what tests would you apply (*a*) to show that they were chlorides, (*b*) to find out which was sodium chloride and which potassium chloride?

8. How is potassium chlorate prepared on the large scale? What are its principal uses?

9. How much sodium chloride is necessary to produce half a ton of sodium hydroxide by the Castner Kellner process?

CHAPTER XXV

CALCIUM

Occurrence

Calcium is not found in the free state in nature, but it occurs very abundantly in the earth's crust, chiefly as **calcium carbonate,** $CaCO_3$, which is found in the forms of limestone, chalk, marble, calcite, Iceland spar, sea shells, coral, pearls, etc. Dolomite contains calcium carbonate and magnesium carbonate.

Other calcium compounds found in nature are **calcium sulphate,** which occurs as gypsum and alabaster, $CaSO_4 \cdot 2H_2O$, and anhydrite, $CaSO_4$; **calcium phosphate;** and **calcium fluoride** (fluorspar).

Industrial preparation

Calcium is prepared on the large scale by the electrolysis of fused calcium chloride. Calcium chloride, it will be remembered, is obtained in the Solvay process for the manufacture of soda. It is contained in a graphite vessel which acts as the anode. An iron rod serves as the cathode, dipping into the fused calcium chloride (fig. 74). On electrolysis the calcium chloride decomposes into its elements, calcium being deposited at the cathode and chlorine evolved at the anode:

$$CaCl_2 = Ca + Cl_2.$$

As electrolysis proceeds, the iron cathode is raised and the deposited calcium forms a roughly cylindrical stick attached to the iron rod.

Properties

Calcium is a hard metal with a silvery lustre. It possesses typical metallic properties, except that its specific gravity is low for a metal, being 1·6.

A freshly filed surface quickly loses its lustre, becoming covered with a film of calcium oxide:

$$2Ca + O_2 = 2CaO.$$

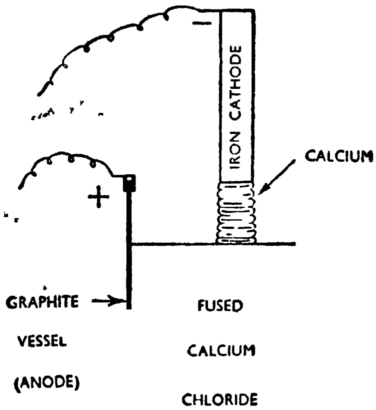


Fig. 74. — Preparation of Calcium

The oxide in turn gradually changes to the hydroxide owing to the action of moisture in the air:

$$CaO + H_2O = Ca(OH)_2.$$

The above reactions are similar to those observed in the cases of potassium and sodium, but with calcium they are much slower, and sticks of calcium are usually kept in airtight bottles or tins, it being unnecessary to have the metal covered with petroleum.

When placed in water, the calcium sinks and bubbles of hydrogen are evolved. The action is less violent than

the similar actions with potassium and sodium. The calcium hydroxide formed partly dissolves in the water, which is found to be alkaline, and a white deposit of excess calcium hydroxide is seen at the bottom of the vessel.

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

Flame test

Calcium and calcium compounds impart a brick-red coloration to a Bunsen flame. The test is carried out in the same way as that for potassium and sodium.

Calcium oxide, quicklime, CaO

Calcium oxide is always prepared by heating the carbonate in a lime-kiln:

$$CaCO_3 = CaO + CO_2.$$

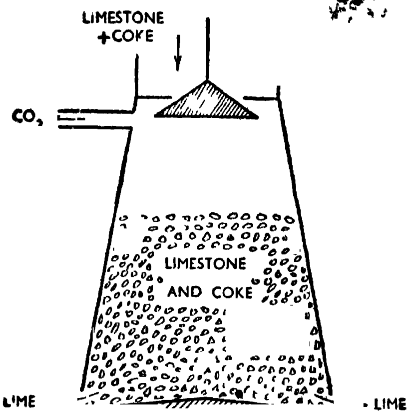


Fig. 75. — Manufacture of Lime

The kiln is filled with a mixture of crushed limestone and coke or coal, and is lit at the bottom (fig. 75). The lime formed is removed at the bottom and a fresh charge

introduced at the top; this goes on indefinitely. The ash from the coal or coke is, of course, mixed with the lime, but this is of no great consequence as it does not affect the mortar or plaster, the making of which constitutes the chief use of lime. When the lime is required pure, the limestone is packed in large lumps in a kiln and is heated by burning producer gas, which enters the kiln at the bottom, the products of combustion leaving at the top with the carbon dioxide from the limestone. Heating continues for two or three days, and then the kiln is emptied. Lime of a high degree of purity results, but the process is considerably more costly than the other.

Calcium oxide is a basic oxide, combining with acids to form salts. It does not melt even when very strongly heated, but it becomes white hot, giving out a bright light known as *limelight*. Its most important property is its reaction with water, with which it combines to form calcium hydroxide. It is used as a drying agent, owing to its strong affinity for water, and in the laboratory it is kept in airtight tins.

Calcium hydroxide, slaked lime, $Ca(OH)_2$

When water is added to a lump of quicklime, great heat is given out, and the quick-lime cracks, swells, and crumbles to a dry white powder. This is calcium hydroxide, slaked lime:

$$CaO + H_2O = Ca(OH)_2.$$

Calcium hydroxide is moderately soluble in water, and a saturated solution is called lime water. This solution is used in the laboratory in testing for carbon dioxide, as described on p. 213.

Lime water is an alkali, turning red litmus blue, and neutralizing acids to form salts.

Slaked lime is a white solid which decomposes when strongly heated, giving quicklime:

$$Ca(OH)_2 = CaO + H_2O.$$

Its chief use is in making mortar. Slaked lime is mixed into a paste with water and sand, and is used in building. On evaporation and absorption of water into the bricks, an intimate mixture of lime and sand is left. The lime is slowly converted into the carbonate by the action of atmospheric carbon dioxide, and this forms a hard crust on the outer surface of the mortar:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Lime is also used in the manufacture of bleaching powder, in softening temporarily hard water, and on the land. Here its application serves to neutralize acids in the soil formed by the decay of animal and vegetable matter. These make the soil "sour" and prevent the nitrifying bacteria from doing their work. In soils where there is no chalk, periodic application of lime is essential for the production of good crops. Lime also helps to break down heavy clay soils and make them more workable.

Portland cement

Portland cement is made by strongly heating a mixture of clay and limestone or chalk. The mixture is fed into the top of a revolving cylindrical furnace sloping slightly downwards. Up the tube is blown a blast of coal dust and air which burns with a hot flame. The resulting "cement clinker", consisting chiefly of calcium silicates and aluminates, is ground into a powder. When mixed with water it slowly sets hard, the reaction being very complex. It is generally mixed with sand and gravel or rubble, the resulting mixture being *concrete*.

Calcium chloride, $CaCl_2$

Calcium chloride, $CaCl_2$, can be made by neutralizing hydrochloric acid with calcium oxide, hydroxide or carbonate. It is produced in large quantities in the manufacture of soda by the Solvay process.

Calcium chloride forms colourless crystals of the

hexahydrate, $CaCl_2 \cdot 6H_2O$, which on moderate heating lose water to form the dihydrate, $CaCl_2 \cdot 2H_2O$. With strong heating, the familiar porous lumps of anhydrous calcium chloride are formed.

The anhydrous salt is used in the laboratory as a drying agent, being strongly deliquescent. It cannot, however, be used for drying ammonia, as it combines with this gas, forming an unstable compound, $CaCl_2 \cdot 8NH_3$.

Calcium chloride solution is used instead of brine in some refrigerators, since it has a low freezing-point and can be circulated as a liquid when very cold.

Calcium sulphate, $CaSO_4$

This occurs as **gypsum**, which is the dihydrate, $CaSO_4 \cdot 2H_2O$. **Alabaster** is a translucent mass of gypsum crystals.

Calcium sulphate is very slightly soluble in water, and is one of the chief causes of " permanent " hardness in water.

When gypsum is heated to between 120° C. and 130° C., it loses three-quarters of its water of hydration, forming the hemihydrate, $(CaSO_4)_2 \cdot H_2O$. This is known as **plaster of Paris.** When plaster of Paris is mixed with water, it rapidly absorbs it, forming the dihydrate, gypsum:

$$(CaSO_4)_2 \cdot H_2O + 3H_2O = 2CaSO_4 \cdot 2H_2O.$$

Plaster of Paris is mainly used for supporting broken limbs after they have been set. It is also used for making moulds, as when it combines with water to form gypsum it increases slightly in volume, and so makes a sharp cast.

Precipitated gypsum, made by adding sulphuric acid to calcium chloride solution, is used in glazing paper, and for making blackboard " chalk ".

Calcium carbonate, $CaCO_3$

Quite a lot has been said about calcium carbonate elsewhere, so we shall merely summarize.

DEPOSITS OF "FUR" IN A HOT WATER PIPE AND IN A KETTLE

It occurs as limestone, chalk, etc.

When strongly heated it decomposes, forming calcium oxide and carbon dioxide.

On adding dilute hydrochloric acid, carbon dioxide is evolved, and this is the usual method for preparing the gas.

On adding dilute sulphuric acid, carbon dioxide is evolved, but the action soon stops, as a coating of calcium sulphate prevents acid coming into contact with the calcium carbonate.

On bubbling carbon dioxide through a suspension of calcium carbonate in water (second part of lime water test for carbon dioxide), the solution clears owing to the formation of calcium bicarbonate.

Hardness in water

Hardness in water is the inability to make a lather easily with soap. Hard water feels rough to the touch. The hardness is due to the presence of calcium salts (and to a lesser degree magnesium salts) in solution in the water. There are two types of hardness, *temporary hardness*, removed by boiling the water, and *permanent hardness*, remaining after the water has been boiled.

Temporary hardness is due to calcium bicarbonate present in the water. Rain-water absorbs carbon dioxide from the air as it falls. More carbon dioxide is absorbed as it passes through the soil. When this water containing carbon dioxide in solution passes over chalk or limestone, the bicarbonate is formed, just as carbon dioxide bubbled through a suspension of calcium carbonate in water forms the bicarbonate:

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

In time large caves are formed in limestone districts through this action.

As we have said, temporarily hard water is that water which is softened by boiling. This is due to the decom-

position of the calcium bicarbonate, the carbonate being precipitated:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

(It is to be noted that the water is soft because the calcium salt is no longer in solution; its presence as precipitated solid ($CaCO_3$) does not cause hardness. The calcium salts react with soap only when they are in solution.)

This precipitated calcium carbonate formed when temporarily hard water is boiled is a nuisance, for it adheres firmly to the insides of kettles, boilers, and hot-water pipes. The " fur ", as it is called, causes great wastage of fuel, for each time a kettle or boiler has to be heated a great amount of heat has to be used up in heating up the fur. Badly furred hot-water pipes greatly hinder the circulation of hot water through the radiators. In districts where the water is temporarily hard it is essential to have the household boilers " scaled " regularly, or to soften the water.

Permanent hardness is due to a straightforward solution of a calcium salt (or, in some places, a magnesium salt) in the water. The chief offender is gypsum, $CaSO_4$, which is slightly soluble in water, and occasionally Epsom salt, $MgSO_4$. Boiling will not soften this water, for the salts will still be in solution at the boiling-point; but in a boiler where water is boiled (as distinct from a household " boiler " where water is not boiled), as water is turned into steam a deposit of calcium sulphate forms a " scale " on the wall.

Water may have both temporary and permanent hardness, and this is often the case. The boiler scale then consists of a mixture of calcium carbonate and calcium sulphate.

Comparison of hardness of samples of water

Some very hard water can be made by bubbling carbon dioxide through lime water until the cloudiness has

disappeared. The water now contains calcium bicarbonate, so the hardness is temporary. Some permanently hard water can be made by shaking up gypsum with water and filtering.

We can compare the hardness of the two samples of water prepared as above, and also of tap water and distilled water.

First it is necessary to make a suitable soap solution. This can be done by dissolving about 6 gm. of pure Castile soap, or good soap flakes, in 100 c.c. of methylated spirit and warming over a water bath to hasten solution.

The soap solution is placed in a burette, and 25 c.c. of the water to be tested is introduced into a soap shaker or conical flask, using a pipette (fig. 76). Soap solution is added from the burette, a little at a time, shaking after each addition, until a " permanent " lather, that is, one which lasts for two minutes, is obtained.

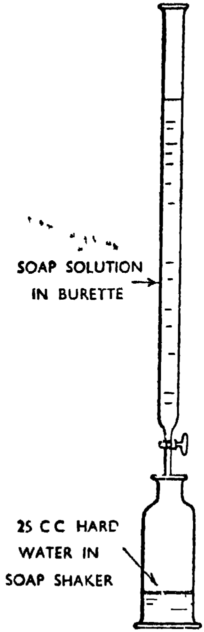


Fig. 76. — Comparison of Hardness of Samples of Water

The hardnesses of the different samples of water are proportional to the volumes of soap solution necessary to produce a permanent lather in each case.

The temporarily hard water may be boiled, and its hardness compared with the hardness before boiling. Hard water softened by any of the methods described below may be compared with the unsoftened sample.

Methods of softening hard water

Temporary hardness can be removed by boiling or by adding lime, or by the same methods as are used for softening permanently hard water.

(i) **By boiling.** — This is impracticable on a large scale.

(ii) **By adding lime.** — This is known as *Clark's process*, and is carried out at the waterworks. The calcium hydroxide reacts with the calcium bicarbonate and forms the insoluble carbonate. This, being out of solution, cannot make the water hard:

$$Ca(OH)_2 + Ca(HCO_3)_2 = 2CaCO_3 + 2H_2O.$$

A little less than the calculated quantity of lime is added; if excess of lime were added, that would dissolve, making the water hard again.

Both temporary and permanent hardness may be removed by the following methods:

(i) **By adding soap.** — Soap consists of sodium salts of certain organic acids, and we may take as example *sodium stearate.* We shall not bother about its formula, but call it $Na\overline{St}$, where $\overline{St}$ stands for stearate, the acid radical of the salt. The soap reacts with any calcium (or magnesium) salts in solution, forming the insoluble *calcium stearate* (or magnesium stearate):

e.g. $$CaSO_4 + 2Na\overline{St} = Na_2SO_4 + Ca\overline{St}_2,$$

and $$Ca(HCO_3)_2 + 2Na\overline{St} = 2NaHCO_3 + Ca\overline{St}_2.$$

The precipitate of calcium stearate may be observed as a white scum (or perhaps it is not always white!) on the surface of the water, and sticking to the sides of the wash basin or bath. Once all the calcium in solution has been precipitated as calcium stearate. and not until then, can the soap get on with its job of producing a lather.

Softening by soap is an expensive business, and laundries and households soften their water by other processes and save soap.

(ii) **By adding washing soda.** — Washing soda, sodium carbonate, precipitates the calcium as calcium carbonate:

$$\text{e.g.} \qquad CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3,$$

$$\text{and} \quad Ca(HCO_3)_2 + Na_2CO_3 = 2NaHCO_3 + CaCO_3.$$

Care must be taken, however, in the use of soda, as it is harmful to the skin. Excess, therefore, should not be used.

(iii) **The Permutit process.** — " Permutit " is the name given to certain salts akin to natural minerals called zeolites. They may be considered to be compounds of the type of *sodium aluminium silicate*, $Na_2Al_2Si_2O_8$, together with water of hydration. We can write this as $Na_2\bar{P}$. (The line over the top of the P will remind you that it stands for " permutite ", and not phosphorus.)

The hard water passes through a cylinder packed with crystals of sodium permutite, and the calcium salts in the water are precipitated as calcium permutite:

$$\text{e.g.} \qquad CaSO_4 + Na_2P = Na_2SO_4 + CaP,$$

$$\text{and} \qquad Ca(HCO_3)_2 + Na_2P = 2NaHCO_3 + Ca\bar{P}.$$

Thus the crystals of sodium permutite are gradually changed on their surface to calcium permutite.

Obviously there is a limit to the softening capacity of such an apparatus, and when it no longer softens the water, the calcium permutite can be changed back to sodium permutite by slowly running strong brine through the apparatus:

$$Ca\bar{P} + 2NaCl = Na_2\bar{P} + CaCl_2.$$

The very soluble calcium chloride is run to waste, and the softener is ready for use again.

Stalactites and stalagmites

Stalactites are " icicles " of calcium carbonate that hang down from the roofs of limestone caves, and stalagmites are the pillars that grow up from the floor of the caves and eventually meet the stalactites. They are caused in the following way: water containing calcium

bicarbonate in solution slowly drips from the roof of a cave, and in doing so a very little evaporates, some of the bicarbonate decomposes, and a very little calcium carbonate is precipitated. Similarly, as the drop is falling through the air, a little more evaporation of water and consequent decomposition of the bicarbonate occur, and so more calcium carbonate is precipitated. Thus a column of precipitated calcium carbonate grows down from the point where the drops leave the roof, and another column grows up from where they land.

The rate of growth of stalactites and stalagmites varies considerably, but it is always very slow.

Stalactites can sometimes be seen hanging down from arches under old brick bridges. Rain-water percolates through, and this, containing carbon dioxide, dissolves a little of the calcium carbonate formed by decomposition of mortar. The resulting calcium bicarbonate solution gives rise to stalactites in the same way as previously described.

QUESTIONS

1. How is calcium prepared on the large scale?

2. Describe the principal properties of calcium.

3. How are quicklime and slaked lime prepared? What are their chief uses?

4. What is gypsum? What happens when (*a*) gypsum is heated moderately, (*b*) water is added to the product?

5. What is meant by "hardness" in water? Explain how natural water may exhibit temporary or permanent hardness.

6. How would you compare two samples of water to ascertain their relative hardness?

7. Describe three good methods by which hard water may be softened.

8. What are stalactites and stalagmites? Explain how they are formed.

9. What weight of calcium carbonate will be precipitated by the addition of two ounces of washing soda crystals to hard water?

CHAPTER XXVI

IRON

Occurrence

Iron does not occur to any great extent in the free state in the earth's crust, although meteorites consist largely of metallic iron.

In combination, iron occurs as **hæmatite,** which is an impure form of ferric oxide, Fe_2O_3, and is the principal ore of iron. Other important ores of iron are **magnetite,** ferroso-ferric oxide, Fe_3O_4, and **spathic iron ore,** ferrous carbonate, $FeCO_3$. **Iron pyrites,** FeS_2, the brassy-looking matter often seen in coal, occurs abundantly, but is not used as an ore of iron. Iron pyrites is, however, used as a source of sulphur in the manufacture of sulphuric acid, and the ferric oxide left after the roasting of the pyrites is used as a source of iron.

Extraction of iron

The ore is first roasted in air, when ferric oxide, Fe_2O_3, is formed, whether the ore is hæmatite, magnetite, or spathic iron ore.

The impure ferric oxide is mixed with coke and limestone and introduced into the top of a blast furnace. The blast furnace is a tall kiln about 100 feet high, made of iron, with a firebrick lining. Hot air is blown in at the bottom through tubes called *tuyères* (fig. 77).

We will leave the action of the limestone until we have seen how the iron is obtained. This is as follows:

The hot air, entering from the tuyères, causes the coke to burn:

$$C + O_2 = CO_2.$$

This carbon dioxide is reduced to carbon monoxide as it passes up through the white-hot coke:

$$CO_2 + C = 2CO.$$

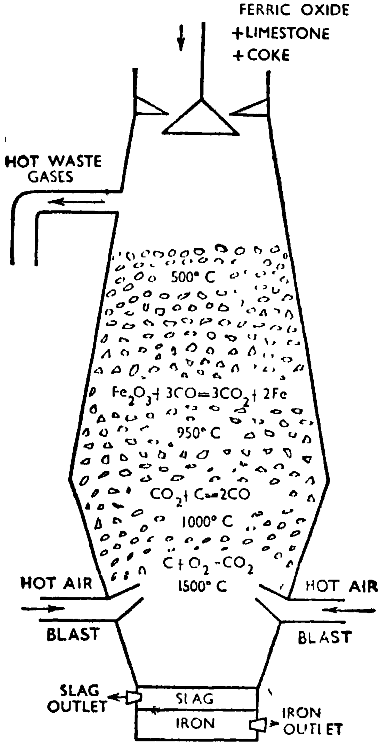


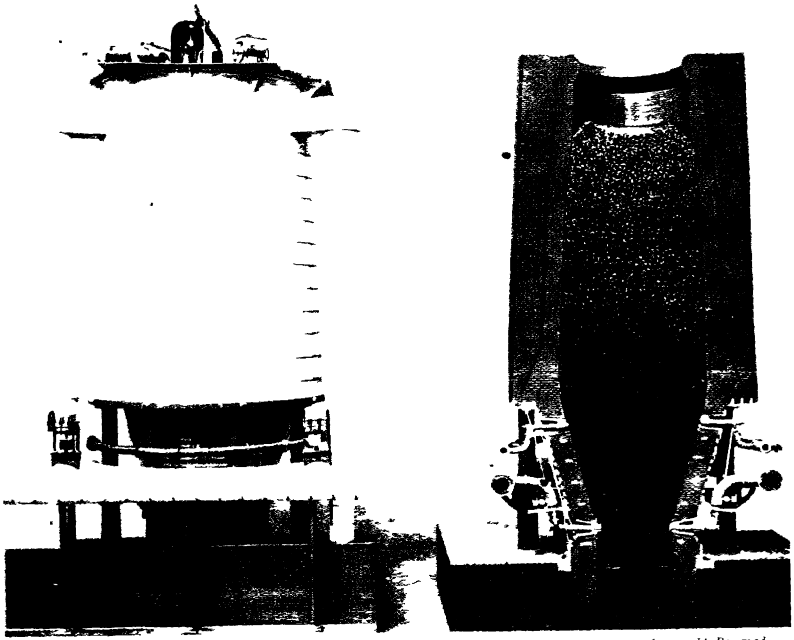
Fig. 77. — Diagram of Blast Furnace

The carbon monoxide so formed reduces the ferric oxide to iron:

$$Fe_2O_3 + 3CO = 3CO_2 + 2Fe.$$

The iron melts and runs down to the well at the bottom of the furnace, and the liquid iron is tapped

SECTIONAL MODEL
OF A BLAST FURNACE



(In the Science Museum, London. Crown Copyright Reserved.)

off at intervals and is run into moulds, where it solidifies as **pig iron.**

Some of the hot gases evolved at the top of the blast furnace are mixed with air and burnt and used for heating the air for the blast.

Formation of the slag

Limestone is introduced into the top of the furnace with the ore and coke to get rid of the earthy matter and silica in the ore, which would otherwise accumulate in the furnace. As it is, they are removed as a fusible slag, and the process continues for years, the mixture being introduced at the top of the blast furnace and slag and molten iron being run off from the bottom. The action of the limestone is as follows.

The limestone decomposes at the top of the furnace, forming quicklime:

$$CaCO_3 = CaO + CO_2.$$

The quicklime combines with silica present, forming calcium silicate, which is fusible at that temperature:

$$CaO + SiO_2 = \underset{\text{(calcium silicate)}}{CaSiO_3}.$$

Other earthy impurities mix with this and the molten slag runs down to the well and lies on top of the molten iron, and is continually run off. Slag used to be piled up into great hills (slag heaps), but uses are now found for it, principally in road-making.

Cast iron

The pig iron obtained from the blast furnace is cast iron. It contains quite a lot of carbon — as much as $4\frac{1}{2}$ per cent — and some silicon, phosphorus, and sulphur. These impurities render the iron unsuitable for most purposes where strength is needed, for they cause the iron to be very brittle. It makes good castings, however, as it increases slightly in volume on solidifying and

fills up all the crannies and makes a " sharp cast ". It cannot be welded.

Cast iron has a melting-point considerably below that of pure iron.

Wrought iron

This is the purest form of iron, and is made from pig iron by oxidizing the impurities in a process known as *puddling*.

The oxidizing agent used is ferric oxide, just sufficient of which is added to the molten pig iron in a furnace. The harmful impurities, phosphorus and sulphur, and also the carbon, form gaseous oxidation products, and so are removed. The resulting wrought iron is 99 per cent pure iron.

Wrought iron is malleable and can be welded. It is used by blacksmiths for horse-shoes and ornamental ironwork, and for making cores of electromagnets. It cannot be tempered, and is too soft for making machinery parts.

Steel

Steel consists of iron which contains a small amount of carbon (from 0·3 to 1·5 per cent). Other substances are also added, according to the purpose for which the steel is being made. The carbon in steel is in the form of iron carbide, Fe_3C.

Steel is mostly made by the Siemens-Martin process. Pig iron, together with scrap iron and ferric oxide, are melted in an open hearth lined with a mixture of calcium and magnesium carbonates in the *basic* process. (In the *acidic* process, sometimes used, the hearth lining is made of siliceous materials.) The furnace is heated by burning previously heated producer gas. The carbonates in the hearth lining decompose to form calcium and magnesium oxides. These oxides, being basic, combine with the acidic oxides formed by the oxidation of the

phosphorus and sulphur, forming calcium and magnesium phosphates and sulphates. Sufficient ferric oxide is added to remove the phosphorus and sulphur and some of the carbon, which escapes as carbon monoxide; the amount of carbon left is carefully regulated, and is determined by the type of steel required. Metals may be added, to form the various alloy steels.

The slag resulting from the open-hearth process, containing phosphates, is a valuable fertilizer, and is known as **basic slag.**

Properties of steel

The most important property of steel is that it can be **tempered.** If it is heated strongly and suddenly cooled, it becomes hard and brittle, and if subsequently heated carefully, its hardness diminishes and it becomes tougher. So, by carefully reheating quenched steel to a particular temperature, a particular degree of hardness and toughness can be obtained. The great ability of Sheffield steel temperers is due to years of experience.

Alloy steels

These have of recent years become increasingly important.

Manganese steel contains about 12 per cent of manganese, and is very tough and wear-resisting. Hence it is used for bends and points in railway lines, for the tyres of railway engines and coaches, and for safes, etc.

Nickel-chromium steel, containing about 3 per cent of nickel, 1 per cent of chromium, and 0·3 per cent of carbon, has a very high tensile strength, and so is used for making cables, propeller shafts, and various other machine parts.

Stainless steel contains 12 to 15 per cent of chromium, together with a little nickel and 0·3 per cent of carbon.

Many other metals are added to steel in various proportions; for example, tungsten, cobalt, vanadium, and molybdenum. The non-metal silicon is also used. The result is that steels to suit all purposes can be made.

Properties of iron

Pure iron is a fairly soft malleable metal with a bright lustre on freshly polished surfaces. It melts at 1525° C., and has a specific gravity of 7·9. It is magnetic.

One of the most interesting (and one of the most annoying) properties of iron is that it readily rusts in the presence of air and moisture. Rust is mainly hydrated ferric oxide, $Fe_2O_3{\cdot}xH_2O$, but the exact nature of rusting is not definitely understood.

Iron will not rust in dry air, nor will it rust in water from which all dissolved air has been expelled. Hence both air and water are necessary for rusting.

Iron may be protected from rusting by covering it with some substance which is resistant to atmospheric conditions. A smear of petroleum jelly or a coating of black lead (graphite) is often used. Paint protects iron well, but if the paint becomes scratched, the iron rusts. The rusting spreads and forces off the paint.

A common method of protecting iron from rusting is by the process of **tinning.** Tin plate from which "tin" cans are made is sheet iron which has been dipped into molten tin. The tin is not affected by moisture and air, and so remains bright. When the coating of tin becomes worn or scratched, however, the rusting of the iron proceeds, even being accelerated by the presence of the tin.

Galvanized iron consists of iron sheets dipped in molten zinc. This is extremely useful and lasts a long time except in industrial towns. Here the zinc is affected by acids in the atmosphere, and the galvanized iron has a relatively short life.

Compounds of iron

Iron exhibits two valencies. It may be bivalent or tervalent, and so it gives rise to two series of salts. Compounds in which the iron is bivalent are called **ferrous compounds**; those in which it is tervalent are called **ferric compounds.** As ferric compounds contain more of the electronegative element or radical, ferrous compounds are said to be **oxidized** to ferric, and ferric compounds **reduced** to ferrous compounds.

Soluble ferrous compounds give green solutions, while soluble ferric compounds give yellow or brown solutions.

Ferrous and ferric compounds may be distinguished by precipitating the hydroxides by the addition of potassium, sodium, or ammonium hydroxide:

$$\underset{\text{(ferrous sulphate)}}{FeSO_4} + 2NH_4OH = (NH_4)_2SO_4 + \underset{\text{(ferrous hydroxide, green precipitate)}}{Fe(OH)_2}.$$

$$\underset{\text{(ferric chloride)}}{FeCl_3} + 3NH_4OH = 3NH_4Cl + \underset{\text{(ferric hydroxide, brown precipitate)}}{Fe(OH)_3}.$$

A very delicate test for a ferric salt is the addition of potassium thiocyanate solution. A blood-red coloration of ferric thiocyanate is observed in the case of ferric salts:

$$FeCl_3 + \underset{\text{(potassium thiocyanate)}}{3KCNS} = \underset{\text{(ferric thiocyanate)}}{Fe(CNS)_3} + 3KCl.$$

Ferrous salts show no change of colour with potassium thiocyanate. If they are, as is often the case, oxidized to some small extent to ferric salts, a slight reddish coloration will indicate the fact.

Another interesting distinguishing test is afforded by the addition of solutions of potassium ferricyanide and potassium ferrocyanide respectively to ferrous and ferric salts.

Ferrous salts and potassium ferricyanide give a dark blue precipitate of **Turnbull's blue.**

Ferric salts and potassium ferrocyanide give a dark blue precipitate known as **Prussian blue.** You are doubtless acquainted with Prussian blue, which is used as a pigment.

Ferrous oxide, FeO, can be made by passing hydrogen over ferric oxide:

$$Fe_2O_3 + H_2 = H_2O + 2FeO.$$

It reacts with acids, forming ferrous salts and water.

Ferrous hydroxide, $Fe(OH)_2$, is obtained as a green precipitate when potassium, sodium, or ammonium hydroxide is added to a solution of a ferrous salt.

Ferrous sulphate, green vitriol, $FeSO_4$, is the most important ferrous salt. It is formed when iron is dissolved in dilute sulphuric acid:

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Anhydrous ferrous sulphate is a white powder, but the salt is generally met with in the form of green crystals, which consists of the heptahydrate, $FeSO_4{\cdot}7H_2O$. It was called "green vitriol" because of its likeness to green glass.

Ferrous sulphate solution slowly oxidizes in the air, the solution turning brown.

When ferrous sulphate is strongly heated, it decomposes, forming sulphur dioxide and sulphur trioxide, and leaving a red powder of ferric oxide:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

If the crystals are heated and the gases condensed, the water of hydration driven off dissolves the oxides of sulphur. In this way sulphuric acid was originally prepared, and so was called *oil of vitriol.*

Ferrous sulphate is used in making ink. In the laboratory, as we have seen, it is used in the brown ring test for nitrates (p. 144).

Ferrous chloride, $FeCl_2$, may be made by dissolving iron in dilute hydrochloric acid:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2.$$

It forms green crystals of the tetrahydrate, $FeCl_2 \cdot 4H_2O$.

Ferrous sulphide, FeS, may be prepared by heating a mixture of iron and sulphur in the correct proportions by weight. The atomic weights of iron and sulphur are 56 and 32 respectively, and so we may mix, say, 14 gm. of iron filings with 8 gm. of flowers of sulphur. Considerable heat is evolved and a black mass of ferrous sulphide results. The pure substance, free from iron, is a yellowish crystalline mass.

Ferrous sulphide is used in the preparation of hydrogen sulphide, which is given off when it dissolves in dilute acids:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Ferric oxide, Fe_2O_3

Ferric oxide occurs as hæmatite. It may be prepared in the pure state as a red powder by heating ferrous sulphate, as previously described, or by heating ferric hydroxide:

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

With dilute acids it gives ferric salts and water.

Pure ferric oxide is used as a polishing powder (jeweller's rouge) and for making red paint.

Hæmatite is used in the production of iron.

Ferric hydroxide, $Fe(OH)_3$, is obtained as a reddish-brown gelatinous precipitate when potassium, sodium, or ammonium hydroxide solution is added to a solution of a ferric salt.

Ferric chloride, $FeCl_3$, can be obtained by passing chlorine over heated iron. It is a blackish solid, and crystallizes from water as the yellow hexahydrate, $FeCl_3 \cdot 6H_2O$.

Ferroso-ferric oxide, Fe_3O_4

This oxide, occurring naturally as magnetite, can be regarded as a compound of ferrous and ferric oxides, i.e. $FeO \cdot Fe_2O_3$. It is a black powder, and is formed when iron is burnt in air or oxygen. It can be seen as scales on the floor of a blacksmith's shop:

$$3Fe + 2O_2 = Fe_3O_4.$$

It is also formed when steam is passed over red-hot iron:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Its nature as a compound of ferrous and ferric oxides is shown in its reactions with acids, when it forms a mixture of ferrous and ferric salts:

e.g. $Fe_3O_4 + 4H_2SO_4 = FeSO_4 + Fe_2(SO_4)_3 + 4H_2O.$

If we regard Fe_3O_4 as $FeO \cdot Fe_2O_3$, we get the two reactions:

$$FeO + H_2SO_4 = FeSO_4 + H_2O.$$
$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O.$$

These two equations added together give the one above. Ferroso-ferric oxide is magnetic; pieces of magnetite were used in olden times as primitive compasses, and were called *loadstones*.

Iron disulphide, FeS_2, is important because it occurs naturally as **iron pyrites**, and is used in the manufacture of sulphuric acid.

QUESTIONS

1. Describe the extraction of iron from iron ore.

2. What are the physical properties of pig iron and wrought iron? State their uses and disadvantages.

3. What is steel? Explain how steel is made from pig iron.

4. What properties of steel cause it to be so important?

5. What happens when iron rusts? Describe briefly two methods in common use for protecting iron from rusting.

6. What tests would you apply to ascertain whether a given iron salt is a ferrous or a ferric compound?

7. How would you prepare a sample of pure ferric oxide?

8. How is ferroso-ferric oxide formed? What are its chief properties?

CHAPTER XXVII

COPPER

Occurrence

Copper, a metal low in the electrochemical series, is found in the free state in some places, and is easily isolated from its compounds. Copper and bronze have for that reason been known from very early times.

Large quantities of native copper are found near Lake Superior, but the chief source of the metal is **copper pyrites**, $Cu_2S{\cdot}Fe_2S_3$, which is found in large quantities in the American continent, and in Australia and Europe Other important ores of copper are the green mineral **malachite**, $CuCO_3{\cdot}Cu(OH)_2$, and **azurite**, $(CuCO_3)_2{\cdot}Cu(OH)_2$, which, as its name suggests, is blue.

Extraction of copper

Native copper is often extracted electrolytically, by erecting a wall around a boulder of impure metal and filling the space with acidified copper sulphate solution. A sheet of copper placed in the solution serves as the cathode, while the copper boulder makes the anode of an electrolytic cell. On passing a current of electricity through this cell a deposit of pure copper is made at the cathode. There is no need in this process for further refinement.

The extraction of copper from copper pyrites, however, presents a more difficult problem, as iron sulphide is present in the ore as well as copper sulphide. However, iron sulphide is more easily oxidized to oxide than is the copper sulphide, and after somewhat complicated preliminary processes, the purified mixture of sulphides is placed together with some silica in a steel " converter "

lined with magnesite, and air is blown through. The iron sulphide is oxidized to the oxide, and this combines with the silica to form a fusible slag of ferrous silicate, $FeSiO_3$.

The slag is run off and air is blown in again, when some of the cuprous sulphide is oxidized to cuprous oxide:

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2.$$

The cuprous oxide thus formed reacts with the remainder of the cuprous sulphide to form copper:

$$2Cu_2O + Cu_2S = SO_2 + 6Cu.$$

The copper is poured off and is known as " blister copper ". It contains some cuprous oxide, and is purified to some extent by stirring the molten metal with green wood (" poling "), when the gases given off from the sap of the green wood reduce the cuprous oxide to copper.

The copper so formed is refined electrolytically by using the copper as anodes in a cell with acidified copper sulphate as the electrolyte. The cathodes consist of strips of pure copper covered with graphite.

Gold and silver, present as impurities in the crude copper, remain in the anodes, and are recovered.

Properties

Copper is a lustrous reddish metal which can take a high polish. It is malleable and ductile and is an extremely good conductor of heat and electricity. The presence of impurities, however, considerably reduces its electrical conductivity, and so copper used for electrical purposes must be refined. It has a specific gravity of 8·95, a melting-point of 1100° C., and it boils at 2320° C.

Copper is unaffected by dry air or pure water, but in the atmosphere it becomes covered with a green coating,

said to be a basic sulphate. Near the sea, the coating on exposed copper contains also a basic chloride.

On heating in air copper becomes slowly coated with the black cupric oxide, CuO.

The metal is stable to water, steam, hydrochloric acid, and dilute sulphuric acid.

On heating with concentrated sulphuric acid, sulphur dioxide is liberated:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Other reactions also occur here, cuprous and cupric sulphides being formed, making the residue in the flask black.

The action with dilute nitric acid depends on the concentration. With moderately dilute acid, nitric oxide is formed:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

With the concentrated acid, the main gaseous product is nitrogen peroxide:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

Uses of copper

Pure copper is used as a conductor of electricity, being the best conductor next to silver, which would be too expensive. It is also used for steam pipes and boiler parts, as steam has almost no action on it and it is a good conductor of heat. It is also used for ornamental work.

Alloys of copper are extremely useful, the chief ones being brass (copper and zinc) and bronze (copper and tin). "Copper" coins are made of bronze, and "silver" coins contain, besides silver, copper, zinc, and nickel.

Compounds of copper

Copper exhibits two valencies and so forms two series of salts, **cuprous** compounds, where the copper is univalent, and **cupric** compounds, where it is

bivalent. Cuprous compounds are not very important for us at this stage.

Cupric oxide, CuO, is generally referred to as copper oxide. It can be formed by strongly heating copper in air or oxygen.

It is better prepared from copper, however, by first dissolving the metal in nitric acid and then heating the resulting copper nitrate:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

It may also be prepared by heating copper hydroxide, as described below.

Copper oxide is a black powder and is somewhat hygroscopic. It dissolves in acids, giving cupric salts.

Cupric hydroxide, $Cu(OH)_2$, is formed by the addition of sodium hydroxide solution to a solution of a cupric salt, and appears as a pale blue gelatinous precipitate:

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2.$$

If the suspension is boiled, the cupric hydroxide decomposes, forming a black solid, hydrated cupric oxide, of the composition $(CuO)_4{\cdot}H_2O$. If this compound is heated to redness, cupric oxide, CuO, is formed.

Cupric sulphide, CuS, is formed as a black precipitate when hydrogen sulphide is bubbled into a solution of a cupric salt. This fact is used in detecting copper in qualitative analysis:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

Cupric sulphate, blue vitriol, $CuSO_4$, is the compound of copper with which you are doubtless best acquainted. It may be prepared in the laboratory by the action of dilute sulphuric acid and copper oxide. Excess of the insoluble oxide is used, and when the solution is no longer acid to litmus, it is filtered and the copper sulphate crystallized as blue parallelogram-shaped crystals.

Copper sulphate is prepared on the large scale by heating copper with dilute sulphuric acid and blowing air through the mixture:

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O.$$

The familiar blue crystals consist of the pentahydrate, $CuSO_4 \cdot 5H_2O$, and these, on gentle heating, lose water to form the anhydrous salt, which is white. Anhydrous copper sulphate readily combines with water to give the hydrate, and so it is used as a test for water, small traces of which impart a blue colour to the white powder. The more expensive watertight boots are tested by dusting them internally with the white anhydrous powder, standing them in water, and rejecting any that show formation of the blue hydrate.

Copper sulphate is poisonous, and is used by horticulturists to destroy moulds and fungi. Louis Pasteur advocated its use for curing grape disease, and it is still used for this purpose, generally as *Bordeaux mixture.* Bordeaux mixture is made by mixing copper sulphate and lime, when basic copper sulphate is formed. In this country it is used as a spray for potatoes. An alternative spray, and an easier one for home preparation, is basic copper carbonate, made by mixing copper sulphate solution with washing soda solution. This is known as *Burgundy mixture.*

Cupric chloride, $CuCl_2$, can be prepared as green crystals of the dihydrate, $CuCl_2 \cdot 2H_2O$, by dissolving cupric oxide in dilute hydrochloric acid. It is also formed when chlorine is passed over gently heated copper. The anhydrous salt, a brownish-yellow substance, can be made by gently heating the dihydrate, or by heating it in a stream of hydrogen chloride.

On heating, cupric chloride decomposes, forming cuprous chloride, and giving off chlorine:

$$2CuCl_2 = 2CuCl + Cl_2.$$

Cupric nitrate, $Cu(NO_3)_2$, is obtained as deep blue

crystals of the trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$, by dissolving the metal or oxide in dilute nitric acid and evaporating.

On heating it decomposes, forming cupric oxide:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

Tests for copper salts

Solutions of copper salts give a black precipitate when hydrogen sulphide is passed through them.

Ammonia added to solutions of copper salts produces a deep blue coloration. This is a very delicate test.

Copper compounds impart a green coloration to a Bunsen flame. The chloride, however, colours the flame greenish-blue.

QUESTIONS

1. How is pure copper obtained from native boulder copper?

2. Describe the extraction and purification of copper from copper pyrites.

3. What are the chief physical and chemical properties of copper?

4. How would you prepare (*a*) cupric hydroxide, (*b*) cupric oxide, (*c*) cupric sulphate crystals, starting from copper?

5. What are the principal properties and uses of cupric sulphate?

6. Certain blue crystals are said to consist of copper nitrate What tests would you apply to verify that the substance is (*a*) a copper salt, (*b*) a nitrate?

7. What weight of cupric oxide is necessary to prepare 10 gm. of cupric sulphate crystals?

CHAPTER XXVIII

MAGNESIUM: ZINC

MAGNESIUM

Occurrence

Magnesium, occurring high in the electrochemical series, is a very reactive metal and does not occur native. In combination, however, it is very abundant, **dolomite**, $CaCO_3 \cdot MgCO_3$, forming vast mountain ranges. Many other minerals containing magnesium are known, the metal occurring chiefly in the form of carbonate, sulphate, or chloride. **Epsom salt** is magnesium sulphate, $MgSO_4 \cdot 7H_2O$, and occurs in the water at certain spas.

Extraction of magnesium

The preparation of magnesium by reduction of its oxide with sodium is no longer used. It is now extracted by electrolysis of fused anhydrous magnesium chloride, $MgCl_2$, mixed with another compound to lower its melting-point. The electrolysis is performed in an iron pot, heated by a furnace. The pot itself forms the cathode. The anode is graphite. An inert gas (not nitrogen, otherwise magnesium nitride, Mg_3N_2, would be formed) is led over the surface of the electrolyte to prevent oxidation of the magnesium.

Properties of magnesium

Magnesium is a silvery white metal with a melting-point of 650° C. It is light for a metal, the specific gravity being 1·74.

It is not reacted upon by dry air, but in moist air it soon becomes coated with a layer of oxide. Perhaps the

most interesting property of the metal is that it burns with an intensely bright white light, and so is used for flashlight photography and for flares. The metal will even burn in carbon dioxide, forming the oxide and leaving a deposit of black specks of carbon:

$$2Mg + CO_2 = 2MgO + C.$$

Magnesium dissolves in dilute hydrochloric and sulphuric acids. It will also liberate hydrogen from *very* dilute nitric acid, the acid being too dilute to oxidize the nascent hydrogen.

Compounds of magnesium

Magnesium oxide (magnesia), MgO, is formed by heating the metal in air, or by heating the hydroxide, carbonate, or nitrate:

$$\begin{aligned} 2Mg + O_2 &= 2MgO. \\ Mg(OH)_2 &= MgO + H_2O. \\ MgCO_3 &= MgO + CO_2. \\ 2Mg(NO_3)_2 &= 2MgO + 4NO_2 + O_2. \end{aligned}$$

Magnesium oxide dissolves to a small extent in water, the solution being alkaline, showing the formation of magnesium hydroxide.

Magnesium hydroxide, $Mg(OH)_2$, a white solid, is precipitated by the addition of sodium hydroxide solution to a magnesium salt:

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4.$$

Magnesium sulphate, $MgSO_4$, can be made by dissolving magnesium or its oxide or carbonate in dilute sulphuric acid. It forms colourless crystals of the heptahydrate, $MgSO_4 \cdot 7H_2O$, known as **Epsom salt.**

Epsom salt is used in medicine, and is prepared on the large scale by purification of the mineral *kieserite*, $MgSO_4 \cdot H_2O$.

Magnesium carbonate, $MgCO_3$, occurs naturally

as **magnesite,** and together with calcium carbonate as dolomite. It is, like calcium carbonate, insoluble in water, but with carbon dioxide and water it forms the soluble bicarbonate in the same way as calcium bicarbonate is formed:

$$MgCO_3 + H_2O + CO_2 = Mg(HCO_3)_2.$$

Magnesium bicarbonate, like calcium bicarbonate, is a constituent of temporarily hard water.

ZINC

Occurrence

Zinc does not occur in the free state. The chief ores are **calamine,** zinc carbonate, $ZnCO_3$, and **zinc blende,** zinc sulphide, ZnS.

Extraction of zinc

The first part of the process is to roast the ore in air. Both the carbonate and the sulphide form the oxide:

$$ZnCO_3 = ZnO + CO_2.$$
$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

(Where zinc blende is the ore used, the sulphur dioxide produced is oxidized to sulphuric acid.)

Secondly, the oxide is reduced to the metal, using coal or coke as the reducing agent. The mixture of oxide and powdered coal or coke is placed in rows of fireclay retorts, which are strongly heated by burning producer gas. The zinc oxide is reduced and carbon monoxide given off:

$$ZnO + C = Zn + CO.$$

The carbon monoxide burns with a blue flame at the mouth of the condenser. Zinc collects in the liquid state in the condenser, and " zinc dust ", a mixture of zinc and zinc oxide, collects in an extension to the condenser known as the " prolong " (fig. 78).

Zinc is also extracted by an electrolytic process. The ore is roasted and the resulting zinc oxide is dissolved in dilute sulphuric acid. The zinc sulphate solution thus formed is filtered and subjected to electrolysis,

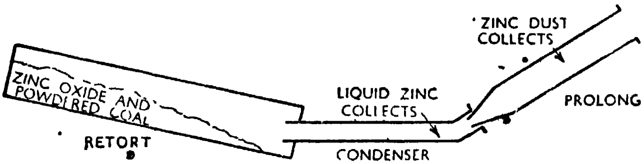


Fig. 78. — Extraction of Zinc

using lead anodes and zinc cathodes. The anode becomes coated with lead dioxide, and zinc of a very high degree of purity is deposited at the cathode.

Properties of zinc

Zinc is a white metal, freshly polished surfaces having a good lustre. It is rather brittle, but becomes malleable and ductile on heating to between 100° C. and 150° C. At higher temperatures it becomes brittle once more. Zinc melts at 420° C. and boils at about 900° C. It has a specific gravity of 7·1.

Zinc is a reactive metal. Freshly polished surfaces quickly tarnish in the air owing to the formation of zinc oxide, the coating of which protects the metal from further oxidation, although the zinc oxide itself slowly changes to basic carbonate. Zinc burns in air when heated, forming the oxide.

Pure zinc does not dissolve in dilute sulphuric acid, although the commercial zinc, containing impurities such as lead, does so readily. This is due to an electrical circuit being set up between the zinc, lead, and acid. If, on preparing hydrogen from zinc and dilute sulphuric acid, the action is very slow, owing to the metal being too pure for the purpose, a few drops of copper sulphate solution poured down the thistle funnel will speed up

the reaction. This causes a deposition of copper on the zinc, and the copper has the same effect as the lead which is in impure zinc.

Zinc (impure) is oxidized by water, if steam is passed over the heated metal. Hydrogen is evolved:

$$Zn + H_2O = ZnO + H_2.$$

Zinc liberates hydrogen from solutions of sodium hydroxide and potassium hydroxide when boiled with them, forming sodium or potassium zincate:

$$Zn + 2NaOH = Na_2ZnO_2 + H_2.$$

Uses of zinc

Zinc is most used in the preparation of galvanized iron. This has already been discussed (p. 260). Zinc is also used in the manufacture of electrical cells; the metal cylinders of dry cells are made of zinc. It is used in the preparation of alloys, and in the extraction of silver and gold.

Compounds of zinc

Zinc oxide, ZnO, may be prepared by heating the metal in air, or by heating the carbonate or nitrate.

Zinc oxide is a white powder, very slightly soluble in water. It dissolves in dilute acids, forming salts, and has the distinctive property of turning yellow when heated; on cooling it goes back to white.

Zinc oxide is used as a white pigment. It is not such a good covering paint as white lead, but it is much less poisonous, and does not darken on exposure to air as lead paint does. This is because zinc sulphide, slowly formed by the action of hydrogen sulphide present in the atmosphere of towns, is white. Lead sulphide, similarly formed, is black.

Zinc hydroxide, $Zn(OH)_2$, is prepared by the

addition of sodium hydroxide or ammonium hydroxide to a solution of a zinc salt:

$$ZnSO_4 + 2NaOH = Na_2SO_4 + Zn(OH)_2.$$

The zinc hydroxide, being but sparingly soluble in water, is obtained as a white precipitate. Excess of hydroxide, however, dissolves it.

Zinc hydroxide decomposes on heating, forming the oxide:

$$Zn(OH)_2 = ZnO + H_2O.$$

Zinc sulphate, white vitriol, $ZnSO_4$, is usually obtained by dissolving the metal in dilute sulphuric acid. It can also be prepared by the other usual methods, that is, from the oxide, carbonate, or hydroxide, and dilute sulphuric acid. On crystallizing from solution, colourless crystals of the heptahydrate, $ZnSO_4 \cdot 7H_2O$, are obtained. On heating these crystals gently, six molecules of water of hydration are driven off. The anhydrous salt is obtained at a higher temperature.

When very strongly heated, zinc sulphate decomposes, forming the oxide and liberating sulphur trioxide:

$$ZnSO_4 = ZnO + SO_3.$$

Zinc sulphide, ZnS, is a white insoluble solid, and is precipitated when hydrogen sulphide is added to a solution of a zinc salt to which ammonium chloride and ammonium hydroxide have been added. Zinc is recognized in qualitative analysis by precipitation of the sulphide in this way.

QUESTIONS

1. What are the chief properties of magnesium?
2. Write a brief account of each of the following: magnesium oxide, magnesium hydroxide, magnesium sulphate, magnesium carbonate.

3. What are the chief ores of zinc? How is zinc extracted from its ores?

4. Describe the chief physical and chemical properties of zinc. What are its principal uses?

5. Describe three ways in which you could prepare crystals of zinc sulphate.

6. Given colourless crystals said to be zinc sulphate, what tests would you apply to verify that the substance is (*a*) a zinc compound, (*b*) a sulphate?

7. What weight of zinc is necessary to prepare two litres of hydrogen at S.T.P., by adding the metal to dilute sulphuric acid?

CHAPTER XXIX

ALUMINIUM: LEAD

ALUMINIUM

Aluminium does not occur uncombined, but it is found abundantly in the earth's crust; clay is hydrated aluminium silicate, together with impurities including free silica. The oxide, **alumina,** occurs as **bauxite,** $Al_2O_3 \cdot 2H_2O$, while another important mineral is **cryolite,** a double fluoride of aluminium and sodium, Na_3AlF_6, which occurs in Greenland. **Corundum** is an impure form of alumina, Al_2O_3.

Extraction

A satisfactory process for the extraction of aluminium from clay has not yet been evolved. The metal is always obtained from bauxite. The bauxite is very carefully purified and then dissolved in fused cryolite. The solution is decomposed by electrolysis, which takes place in an iron vessel lined with carbon, which serves as the cathode. Carbon rods dipping into the molten mass constitute the anode. The fused aluminium collects at the bottom of the cell, whence it is tapped off periodically, while the oxygen liberated at the anode combines with the carbon electrodes to form carbon monoxide.

Properties

Aluminium is a white metal of specific gravity 2·7 and a melting-point of 659° C. It is fairly resistant to atmospheric conditions, the surface becoming coated with a transparent coherent coating of oxide, which

protects the metal from further oxidation. Aluminium is a fairly strong metal and is malleable and ductile. It is a good conductor of electricity.

On heating aluminium in the air, it burns with a bright flame, forming alumina:

$$4Al + 3O_2 = 2Al_2O_3.$$

It dissolves readily in fairly concentrated hydrochloric acid with the liberation of hydrogen:

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

Hot concentrated sulphuric acid dissolves it, when sulphur dioxide is formed:

$$2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 6H_2O + 3SO_2.$$

Nitric acid has no action on aluminium.

Aluminium dissolves on warming in a solution of sodium hydroxide, when sodium aluminate is formed, hydrogen being liberated:

$$2Al + 2NaOH + 2H_2O = \underset{\text{(sodium aluminate)}}{2NaAlO_2} + 3H_2.$$

Aluminium forms a number of useful alloys. **Magnalium,** containing from two to ten per cent of magnesium, and **duralumin,** containing magnesium and copper, are two examples. Magnalium is less dense than aluminium, and is quite strong. Duralumin has a good tensile strength and can be tempered like steel. **Aluminium bronze** contains copper and from three to ten per cent of aluminium; sometimes manganese is added. It is hard and of great tensile strength, and is not corroded by sea water.

Uses

Aluminium and its alloys are used for aircraft construction and for various machine parts, as well as for cooking utensils. The wire is used as an electrical

conductor **Aluminium powder**, made by stamping thin sheets of aluminium, consists of thin flakes of the metal. When used as a paint it has a very high covering power, more so than other paints containing granular particles. It is used largely for covering iron and thus preventing rusting.

Thermit consists of a mixture of aluminium powder and ferric oxide. When ignited, the ferric oxide is reduced by the aluminium, the reaction being very rapid and great heat being evolved:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

The temperature becomes such that the iron melts. The reaction is used for welding steel, the molten metal being run straight from the crucible on to the pieces of steel to be welded.

Aluminium oxide, Al_2O_3, occurring as corundum, is a hard crystalline substance and is used as an abrasive (**emery**). Hydrated aluminium oxide is used to make pigments called **lakes.**

Aluminium sulphate, $Al_2(SO_4)_3$, made from kaolin (a pure form of clay) and sulphuric acid, is used for sizing paper and in other technical processes. **Alum,** a double salt of aluminium sulphate and potassium sulphate, $K_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$, forms well-defined colourless octahedral crystals. It is used in tanning, in the dye industry, and as an astringent.

Bricks, pottery, and porcelain

Bricks are made from clay. The clay used is impure, containing iron oxide, which imparts the red colour to the bricks. For making pottery a much purer clay must be used. It is washed and mixed with finely ground flints and formed on the potter's wheel. It is then dried and fired in kilns. Porcelain is made from pure china clay mixed with silica.

LEAD

Occurrence

The chief ore of lead is **galena**, lead sulphide, PbS, which is a heavy black lustrous mineral. The metal can very easily be extracted, and consequently lead has been in use for thousands of years. Galena occurs to some extent in this country, but is found in larger quantities in North America, Australia, Spain, and Germany.

Extraction

The extraction of lead from galena is by a comparatively simple process. The ore is first roasted in a current of air at a moderate temperature in a reverberatory furnace, when part of the sulphide is converted to the monoxide and part to the sulphate:

$$2PbS + 3O_2 = 2PbO + 2SO_2,$$
$$PbS + 2O_2 = PbSO_4.$$

More galena is then added, the air current is turned off, and the temperature is raised. Under these conditions the galena reacts with both the lead monoxide and lead sulphate, lead being the product in each case:

$$2PbO + PbS = 3Pb + SO_2,$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

The lead, which is in the molten state, is run off, and the impure metal is purified by stirring in contact with air; this oxidizes impurities, which form a scum on the surface. This can be removed.

Properties

Pure lead has a silvery-white lustre, but, when generally met with, it is of a bluish-grey colour. It is a heavy metal, having a specific gravity of 11 4. It is soft, being easily cut by a knife, when its metallic lustre becomes apparent. The bright surface, however, quickly tarnishes. The

metal is plastic, especially when heated, and this fact is utilized in the manufacture of lead piping and wire, which are made by pressing the warmed solid metal through dies. The metal melts quite easily, the melting-point being 327° C. It is a good conductor of heat and electricity.

Lead tarnishes rapidly on the surface in moist air, a protective coating of hydroxide and carbonate being formed. Pure air-free water has no action on lead, but water containing dissolved air reacts with lead, the lead hydroxide formed dissolving appreciably in the water, rendering it poisonous. If the water is slightly hard, however, an insoluble protective coating is formed, and for this reason very soft water is often artificially hardened to prevent the ill effects due to the soft water passing through lead pipes.

Dilute sulphuric and hydrochloric acids do not react with lead, but hot concentrated sulphuric acid behaves in a manner similar to that with copper, lead sulphate and sulphur dioxide being formed:

$$Pb + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_2.$$

Moderately dilute nitric acid dissolves lead readily, forming lead nitrate and liberating principally nitric oxide:

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 4H_2O + 2NO.$$

With concentrated nitric acid, nitrogen peroxide is also formed:

$$Pb + 4HNO_3 = Pb(NO_3)_2 + 2H_2O + 2NO_2.$$

Uses

Lead is particularly useful in the manufacture of water and gas piping, as it is easily bent to shape, and joints are easily made. As sheet lead it is used extensively for roofing. Many lead alloys are useful, for example: solder, type-metal, and pewter. The metal also finds a use as a casing for electric cables, and in accumulators.

Compounds of lead

Lead monoxide, PbO If lead is heated in air the monoxide is formed as a yellow powder called **massicot.** If heated more strongly and the molten oxide allowed to cool, it forms the well-known orange-coloured crystalline form, **litharge.**

Lead monoxide may be reduced to the metal by passing hydrogen over the heated oxide:

$$PbO + H_2 = H_2O + Pb,$$

or by heating a mixture of the oxide and carbon:

$$PbO + C = CO + Pb.$$

Lead monoxide behaves normally to dilute acids, salts and water being formed, e.g.:

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Litharge is used in the manufacture of flint glass, in glazing pottery, and in the preparation of red lead and lead salts.

Red lead or minium, Pb_3O_4. This oxide, a bright red crystalline powder, is formed by roasting litharge in a current of air at 400° C. At higher temperatures the red lead changes back to litharge. Red lead is used as a pigment, being particularly useful because it covers well and helps to "harden" the oil.

Lead dioxide, PbO_2. Lead dioxide is a chocolate-coloured powder made by the oxidation of red lead by nitric acid. It is a good oxidizing agent; for example, it oxidizes hydrochloric acid to chlorine:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

Lead chloride, $PbCl_2$. Lead chloride is a white crystalline solid, easily soluble in hot water but only slightly soluble in cold water. It can, therefore, be conveniently prepared by the addition in the cold of hydrochloric acid or a chloride to a solution of a lead salt, the lead chloride being precipitated:

$$Pb(NO_3)_2 + 2HCl = 2HNO_3 + PbCl_2.$$

Lead nitrate. $Pb(NO_3)_2$. Lead nitrate may be prepared by dissolving lead, litharge, or lead carbonate in nitric acid. It is soluble in water and crystallizes without water of hydration. On heating lead nitrate it decomposes, nitrogen peroxide and oxygen being given off:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

White lead. This well-known pigment is a basic carbonate of lead, having the composition $2PbCO_3 \cdot Pb(OH)_2$, and is formed when a solution of sodium carbonate is added to a solution of a lead salt. It is manufactured by placing rolls of lead in earthenware pots with vinegar at the bottom. These pots are stacked in rows with layers of tan bark or dung between the rows. The fermentation of the tan bark causes carbon dioxide to be liberated, and this carbon dioxide decomposes the basic lead acetate formed from the vinegar and the lead, the result being white lead.

White lead is opaque and has a good covering power, and is largely used for making paints, colouring matter being added to the white lead paint to produce the colour required. White lead paint gradually darkens in the atmosphere, hydrogen sulphide present in the air slowly changing it to lead sulphide, which is black.

QUESTIONS

1. In what forms does aluminium occur in the earth's crust? Describe how the metal is extracted from one of them.

2. Write an account of the principal properties and uses of aluminium and its alloys.

3 Describe the extraction of lead from galena. What are the principal uses of lead?

4. What are the chief physical properties of lead? Describe the reactions of lead with (*a*) air, (*b*) water, (*c*) sulphuric acid, (*d*) nitric acid.

5. Write a brief account of the oxides of lead. How would you prepare specimens of lead chloride and lead nitrate?

6. Describe the manufacture of white lead. What are its advantages and disadvantages as a pigment?

SYMBOLS AND APPROXIMATE ATOMIC WEIGHTS OF THE MORE COMMON ELEMENTS

Element	Symbol	Approx Atomic Weight	Element	Symbol	Approx. Atomic Weight
Aluminium ..	Al	27	Iron	Fe	56
Antimony ..	Sb	122	Lead	Pb	207
Argon ..	A	40	Magnesium ..	Mg	24
Arsenic ..	As	75	Manganese ..	Mn	55
Barium ..	Ba	137	Mercury ..	Hg	201
Bismuth ..	Bi	209	Nickel	Ni	59
Boron	B	11	Nitrogen ..	N	14
Bromine ..	Br	80	Oxygen ..	O	16
Calcium ..	Ca	40	Phosphorus ..	P	31
Carbon ..	C	12	Platinum ..	Pt	195
Chlorine ..	Cl	35·5	Potassium ..	K	39
Chromium ..	Cr	52	Silicon	Si	28
Cobalt ..	Co	59	Silver	Ag	108
Copper ..	Cu	64	Sodium ..	Na	23
Gold ..	Au	197	Sulphur ..	S	32
Helium ..	He	4	Tin	Sn	119
Hydrogen ..	H	1	Tungsten ..	W	184
Iodine ..	I	127	Zinc	Zn	65

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											Mean Differences								
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											Mean Differences								
50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

ANSWERS TO NUMERICAL EXAMPLES

CHAP. III, p. 25.

3. 56·0 c.c.	5. 51·41 c.c.	7. 36·7 c.c.	9. 57·3° C.
4. 1118 mm.	6. 335·8° C.	8. 1081 mm.	

CHAP. VI, pp. 48–49.

4. 12·0.	7. 62·6.	10. 32.	13. 32·5.
5. 27·7.	8. 32·3.	11. 97·6.	14. 39·2.
6. 61·0.	9. 60.	12. 27·7.	15. 23·0.

CHAP. VII, p. 61.

3. (*a*) C 27·3, O 72·7. (*b*) K 52·2, Cl 47·8.
   (*c*) K 38·6, N 13·9, O 47·5. (*d*) N 21·2, H 6·1, S 24·2, O 48·5.
   (*e*) H 2·0, S 32·7, O 65·3.
4. (*a*) 36. (*b*) 43·9. (*c*) 62·9.
5. (*a*) CO. (*b*) Al_2O_3. (*c*) $CaCO_3$. (*d*) $Ca(OH)_2$. (*e*) $K_2Cr_2O_7$
6. 7·3 gm.
7. 35 tons.
8. $17\frac{6}{7}$ tons.

CHAP. VIII, p. 69.

5. 47·6. 6. 94·3.

CHAP. XI, p. 92.

6. 62·9.

CHAP. XII, p. 108.

2. 1·8 gm.

CHAP. XIII, p. 119.

2. 15·1 gm., 3·45 litres.

CHAP. XIV, p. 127.

12. 3·55 gm.

CHAP. XV, p. 140.

10. 4·78 gm.

CHAP. XVII, p. 166.

11. 83·76 gm.

CHAP. XIX, p. 192.

15. $3\frac{1}{18}$ tons.

CHAP. XXI, p. 220.

11. 4·48 litres.

CHAP. XXIV, p. 242.

9. 0·73 tons.

CHAP. XXV, p. 254.

9. 0·7 oz.

CHAP. XXVII, p. 271.

7. 5 gm.

CHAP. XXVIII, p. 278.

7. 5·8 gm.

INDEX